MULTI-MEDIA MONITORING OF TRACE METALS AND PESTICIDES IN THE BATTLE RIVER 1989-1990

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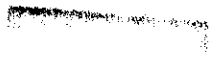

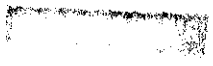

MULTI-MEDIA MONITORING OF TRACE METALS AND PESTICIDES IN THE BATTLE RIVER 1989-1990

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OVERVIEW

The Multi-Media Monitoring Pilot Program on the Battle River was undertaken to assess and compare the suitability of water and other media such as bottom sediments, suspended sediments and biota (plants, invertebrates, and fish) for monitoring heavy metals and pesticides. Development or enhancement of sampling and analytical protocols and evaluation of seasonal and longitudinal trends in contaminant levels were important components of this assessment.

Water was sampled using traditional methods, but also more recently developed techniques such as large volume field extraction using the Goulden and Pressure Container methods. The muddy or sandy bottom of this shallow river was sampled with an Ekman Dredge, and a Sedisamp System was used to collect suspended sediments. Several collection methods were required to sample the biota of the Battle River. Sampling of suspended sediments and large volume extractions required the most expensive field instrumentation and the highest skill level. However, man-power requirements were highest for the collection of invertebrate samples.

Analytical methods for determining Cu, Cr, Ni, V, Zn, As, Se, and Hg in biota and Cd, Pb, Cu, Cr, Co, Ni, V, Zn, As, Se, and Hg in sediment were established as required by this project. Strategies and procedures used for the preparation, extraction/digestion, and analysis of sediment and biota are presented. Analytical techniques used included ICP-AES, Hydride Generation Quartz Furnace AAS and Cold Vapour AAS. These methods were used for the analysis of trace metals in sediment and biota sampled from the Battle River.

The analytical performance of these methods was evaluated in terms of quality control samples analyzed in conjunction with field samples. These quality control samples included certified reference materials, in-house reference materials, spikes and duplicates. This evaluation indicated that, in general, these methods offer results with reasonably good accuracy and precision for most parameters tested. For biota analysis, the precision in the determination of Se needs to be improved and methods for determining Cd and Pb need to be established. Analyses of Se in sediment was biased low and therefore further improvement of this method should be conducted. The accuracy of Hg in sediment could not be evaluated with any certainty, and further investigation into this method is also warranted.

Standard protocols of Environment Canada were used for the determination of phenoxy acid herbicides, neutral herbicides, and organochlorine pesticides (and the non-pesticide total PCBs). Phenoxy acid herbicides were analyzed in water only, while the other target groups were measured in all media.

Although human activity may influence heavy metal concentrations, it was evident that natural factors controlled most of the variability encountered in the Battle River data set.

- Since heavy metals occur naturally in the earth's crust they may be encountered in any component of aquatic systems. Metals were detected in all of the more than 180 samples collected in this study from the six media sampled in the Battle River. However, concentrations of some metals were often below the analytical detection limit in the water samples and fish muscle was the only medium which consistently yielded measurable concentrations of mercury.

- Seasonal and longitudinal changes in total metal levels in water were strongly related to river discharge and non-filtrable residue concentrations. However, dissolved metal concentrations were independent of flow and increased gradually in a downstream direction.

- Metal levels in bottom sediments and suspended sediments were strongly related to the organic content and particle size of the sediments. Higher concentrations of metals were measured at sites in the upper basin; sediment at these sites was finer grained and had more organic matter than sites from the lower basin. Slight, local enrichment, independent of substrate characteristics and possibly related to anthropogenic activities was detected at some sites for lead, copper, and zinc. Seasonality was not apparent in sediment metal levels, nor was consistency in vertical distribution.

- Dynamic physiological processes and inter- and intra- specific differences were among the most obvious factors which affected metal levels in biological samples. Metal concentrations were high in macrophyte roots, low in stems and leaves of these plants and intermediate in filamentous algae. Longitudinal patterns were best defined in stems and leaves and corresponded well to longitudinal patterns in water. This suggests that these plant parts may have a potential value as time integrators of trace metals. Concentrations of metals in invertebrates varied considerably among taxa and among sites. This large variability prevented the detection of longitudinal trends.

  However, variability was low in duplicate samples (same site, same taxon) as long as these samples consisted of a large number of specimens. If these samples consisted of single, large specimens, such as unionid clams, variability was large. Seasonal differences were likely related to metabolic activity and were apparent in the lower concentrations of arsenic, chromium, zinc, and vanadium and the less frequent detections of mercury in fall compared to spring samples. There was little intra- and inter-species variation in fish muscle metal concentration. With the notable exception of mercury, most metals occurred at lower concentrations in fish muscle than in other biological samples.

Whereas the detection of metals in aquatic ecosystems is not necessarily related to human activity, the presence of pesticide residues is. A total of 126 samples were analyzed from different media sampled in the Battle River.

- Samples were analyzed for a multi-residue analytical list including the six highest selling Alberta herbicides, and eight of the top ten. High usage herbicides not analyzed included glyphosate (Roundup) and difenzoquat.

- Highest frequency of detection was found in water. Residues most commonly measured included 2,4-D, MCPA, gamma-BHC, 2,4-DP, dicamba, bromoxynil, and triallate. Detections in water did not correlate significantly with usage.

- Several residues in water displayed significant seasonal (June and July maxima) and longitudinal variability (downstream increased concentration).

- Low recoveries were achieved with the Goulden Large Sample Extractor. A number of changes to techniques were recommended to increase these recoveries, including sample clarification and warming, and reduced flow-through rates. Despite the low recoveries, the informational value of the large sample extracts exceeded that of comparable grab water samples.

- Residue detections in sediment were limited to a single compound (triallate). The study results, combined with findings in the recent literature, suggest that pesticide monitoring can be undertaken efficiently with water and biological media. The role of sediments can likely be limited to special surveys to describe the extent and nature of depositional storage (bottom sediments and event transport suspended sediments). All sediment analyses should include documentation of particle size and organic matter content since these factors are important determinants of residue adsorption.

- Longitudinal and seasonal patterns in biological tissues concentrations were difficult to interpret, largely due to a limited number of detections and to inter-taxa variability. Residues recurrently found in invertebrates, plants and fish included metolachlor, atrazine, and triallate, suggesting that the three media might be equally appropriate for monitoring of neutral herbicides. Uptake and depuration rates can vary between residues and between species, and this should be noted in monitoring design.

- The study results and the availability of comparable databases in the literature suggest that fish tissues are the preferred medium for monitoring of organochlorine/PCBs. Depending upon the specific study objectives, a number of species and tissues-organs might be sampled. A piscivorous species should be chosen if available, and an effort should be made to retain consistency in both species and tissue type.

With a few exceptions, objectives or guidelines for metals and pesticides have been set for the water medium only. In the Battle River cadmium and chromium levels in water regularly exceeded Canadian Water Quality (CCREM) guidelines and the Prairie Provinces Water Board (PPWB) objectives. Guidelines were also exceeded at higher flows for copper,

zinc and nickel and on a single occasion for lead. Even the most lenient sediment guidelines for arsenic were often exceeded, whereas those for mercury were always met. Mercury concentrations in pike and white suckers complied with consumption guidelines for game fish.

Pesticide results in water were compared with the most restrictive water quality objectives which could be found, regardless of jurisdiction. Usually, these objectives were for the protection of sensitive uses such as freshwater aquatic life or drinking water. The majority of detections in water were three or more orders of magnitude below these guidelines. Sum of BHC isomers (alpha plus gamma) approached the CCREM guideline of 10 ng/L during June and July of 1989 at Unwin (6 ng/L total).

Comparison of multi-media metals and pesticide data from the Battle River with the literature were often difficult because of the relative scarcity of such data, the variety of field and analytical methods used, the lack of comprehensive guidelines and objectives for media other than water, and the fact that many studies take place near important point sources of contaminants rather than on a basin-wide basis. A prime concern of future monitoring programs should be to utilize standardized field and laboratory methods to the greatest extent possible to facilitate immediate comparisons of results with those from other studies.

ACKNOWLEDGEMENTS

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1. GENERAL INTRODUCTION

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1.0 GENERAL INTRODUCTION

The chemical and physical properties of water have been monitored more intensively than those of any other component of freshwater ecosystems. The perception of water quality is primarily defined by uses for which the water is intended. This is reflected in guidelines or objectives which define desirable chemical and physical characteristics of water for specific uses (e.g., CCREM 1987). Growing concern about trace levels of contaminants in aquatic ecosystems has led to the refinement of analytical techniques which permit the detection of very low concentrations of contaminants in water; it has also led to a more holistic approach in aquatic environment monitoring. Because other ecosystem components such as sediments or biota may act as permanent or temporary sinks for contaminants, increasing emphasis is being placed on the acquisition of baseline information on contaminant levels in these components, on the identification of pathways of contaminant transfer within and among components, and on the assessment of the environmental significance of particular levels of contaminants.

1.1 BATTLE RIVER MULTI-MEDIA PILOT STUDY

In 1989 a joint study was undertaken by Alberta Environment, Environment Canada, and the Saskatchewan Department of Environment and Public Safety on the Battle River to assess the suitability of various ecosystem components (i.e. media), including water, sediments, and biota, for the monitoring of selected contaminants. The contaminants targetted for analysis were pesticides and metals.

Specific study objectives were to:

1. Develop and select methods for the sampling and analysis of pesticides and trace metals in a small, slow-moving river with sedimentary substrates such as the Battle River.
2. Assess the potential value of various media in the routine monitoring of these contaminants.
3. Evaluate the data from longitudinal and seasonal surveys and assess their potential value in long-term monitoring programs.

This report consists of four sections:

Section 1. The "Introduction", contains an overview of the Battle River Basin characteristics;
Section 2. "Method development and analysis of field samples for trace metals in sediment and biota", deals specifically with analytical methodology for trace metal analysis.
Section 3. "Multi-media study of trace metals in the Battle River"; and
Section 4. "Multi-media study of pesticides in the Battle River" deal with sampling methodology and monitoring results of contaminants for each medium sampled in the Battle River.

1.2 BASIN CHARACTERISTICS

The Battle River is located in East-Central Alberta and West Central Saskatchewan. From its source in Battle Lake, it flows in an easterly direction for approximately 800 km to the Alberta-Saskatchewan border. In Saskatchewan it continues its easterly route for nearly 300 km to its confluence with the North Saskatchewan River, a tributary of the Saskatchewan-Nelson River system (Figure 1.1). At its confluence with the North Saskatchewan River, at the Battlefords, the Battle River drains an area of 30,000 km^2, of which approximately 25,000 km^2 are in Alberta.

Unlike most other major rivers which flow from west to east in Alberta, the Battle River does not originate in the mountains or the

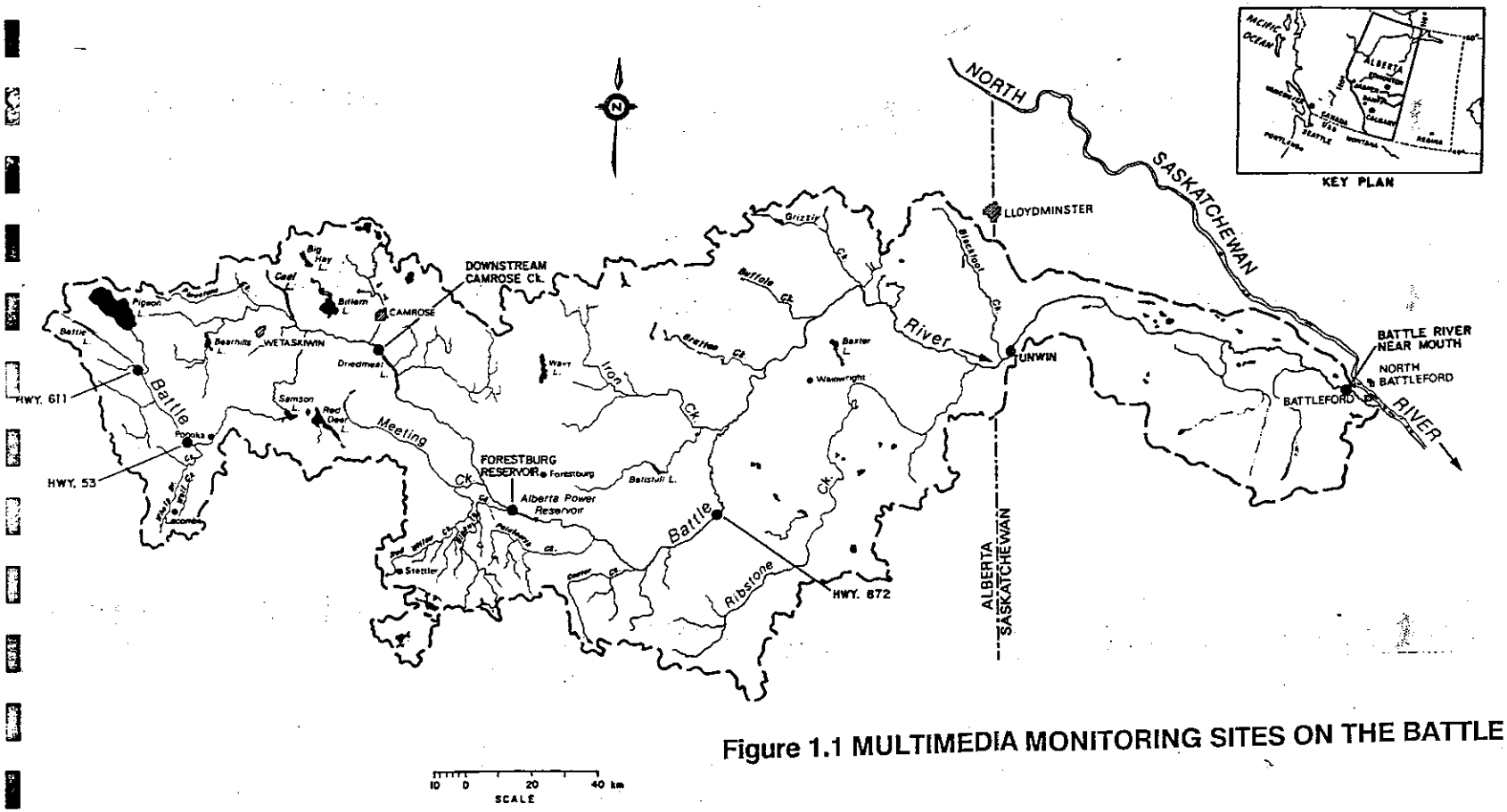

Figure 1.1 MULTIMEDIA MONITORING SITES ON THE BATTLE RIVER (1989-1990)

foothills. Thus, the hydrologic regime in the river is not influenced by mountain snow and glacial meltwater, but by local runoff (spring melt, rain storms), groundwater flow, and supply from lakes and reservoirs (i.e. Battle, Pigeon, Samson, Coal, and Driedmeat lakes and the Forestburg reservoir). Although there are control devices on most of these water bodies, the structure on Coal Lake is the only one which has been operated for flow augmentation. The Forestburg Reservoir provides cooling water for the Alberta Power Ltd. coal-fired power plant. Typically, flows in the Battle River are high in spring, decline rapidly in summer, and remain low through fall and winter (Figure 1.2).

The Battle River flows through two main ecoregions (Strong and Leggat 1981). Battle Lake and the first 10 to 20 km of the river are located in the boreal mixedwood biome characterized by aspen poplar, gray luvisol soils and a boreal climate. The remainder of the basin lies in the aspen parkland biome and is typified by aspen and rough fescue grassland, dark gray and black chernozem soils, and a prairie-boreal climate.

Bedrock geology in the Battle River basin is dominated by Upper Cretaceous and Tertiary Formations with sandstone, shale and coal from the Paskapoo formation upstream of Wetaskiwin; sandstone, shale, coal and minor bentonite from the Edmonton formation in the area between Wetaskiwin and Forestburg; shales and minor sandstone from the Bearpaw Formation between Forestburg and Wainwright; and sandstone, shale, coal and minor bentonite from the Belly River Formation in the lower portion of the basin (Atlas of Alberta 1969).

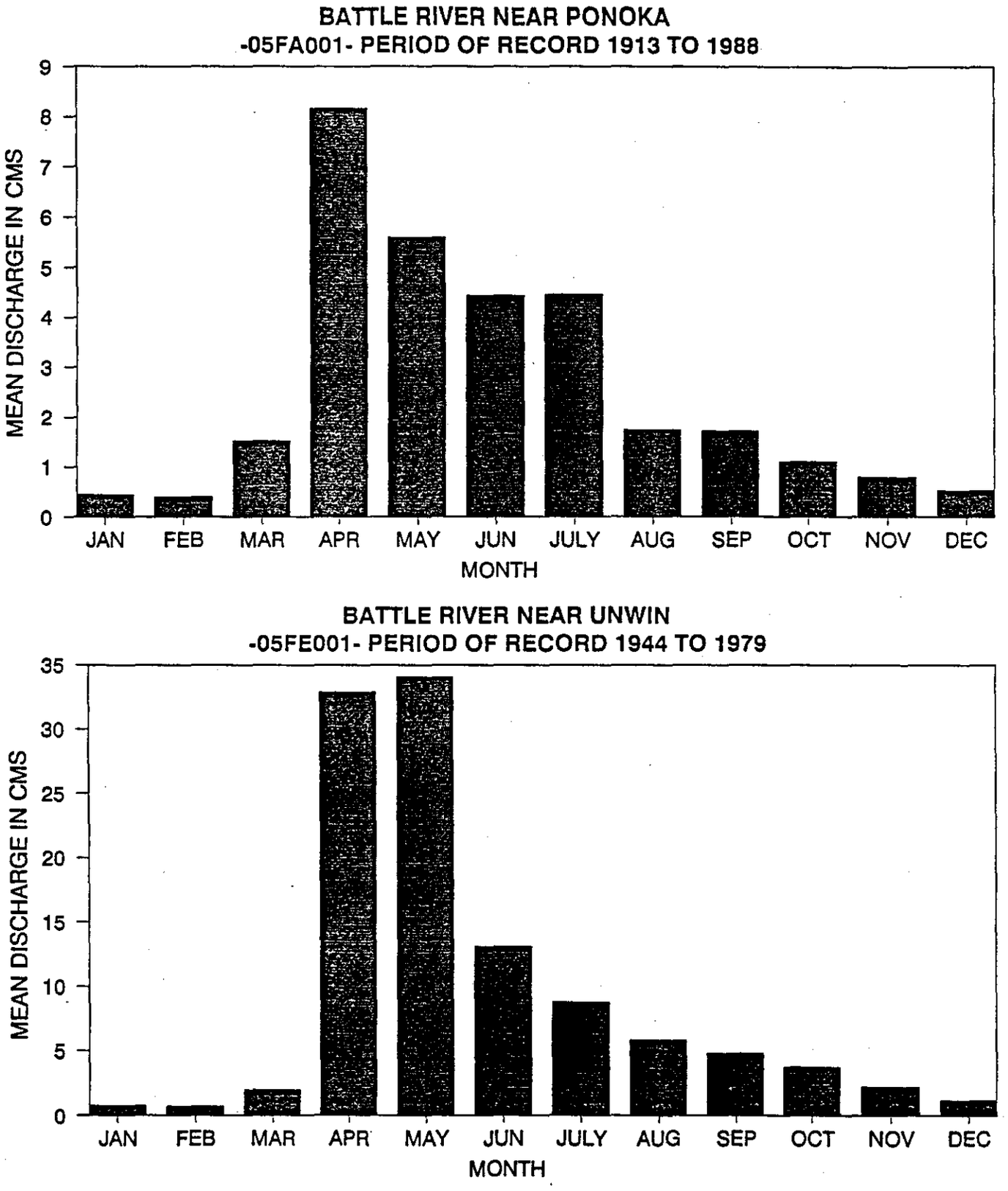

Figure 1.2 MEAN MONTHLY DISCHARGE AT TWO SITES ON THE BATTLE RIVER

Surficial deposits consist mainly of ground moraine and hummocky moraine (till) with outcrops of silt and clay, outwash, lake deposits,and wind deposits of sand and gravel (Atlas of Alberta 1969).

The Battle River basin is rather sparsely populated with a population split almost evenly between urban and rural areas. Stanley Associates Engineering Ltd. (1985) estimated that of the 98,000 inhabitants of the study area in 1983, approximately two-thirds lived in the upper portion of the basin. This distribution is influenced by the proximity to the North-South Alberta transportation corridor and by the relatively higher soil quality in the upper basin.

The economy of the basin is almost exclusively based on agriculture, natural resource industries, and supporting service sectors. Major agricultural crops include wheat, barley, oats, canola and hay; the livestock industry is also important in the basin. There are four large deposits of sub-bituminous coal which represent 18% of the remaining recoverable surface sub-bituminous coal reserves in Alberta (Stanley Associates Engineering Ltd. 1985). Current coal production is mainly in the Paintearth Creek drainage basin, south of the Battle River. The Battle River basin is also a mature oil and gas producing region with ten major producing oil fields either totally or partly contained within the basin.

According to Stanley Associates Engineering Ltd. (1985), the most significant water use in the basin is by Alberta Power Ltd.,representing about 94% of the total licenced use in the basin. The power plant uses the water for cooling purposes and approximately 98% of this water is returned to the river. Other important water uses are

urban (municipal), agricultural, and increasingly, oil-well injection.

The main point-source discharge in the basin is municipal wastewater. The Standards and Approvals Division (Alberta Environment) lists 42 municipalities with licenced wastewater treatment facilities in the basin. Two have continuous discharges (Wetaskiwin to the Battle River, and Wainwright to Bushy Head Lake); 29 discharge to the Battle River or its tributaries in spring and/or fall; 11 have sufficiently large storage capacities and do not discharge.

Industries located in the Battle River basin are listed in Table 1.1 Most of these industries do not have direct discharges to the Battle River. Notable exceptions are Alberta Power Ltd. which discharges ash pond effluent and condenser cooling water to the Forestburg Reservoir and the Luscar Ltd. and Manalta Ltd coal mines which discharge water from settling ponds to Paintearth Creek.

In a study of groundwater quality in the coalmining area south of the Forestburg Reservoir, Trudel (1988) showed that mine spoil ground water was significantly more saline than groundwater typical of pre-mining conditions. Arsenic, boron, copper, cobalt and lead were also commonly detected in this mine spoil groundwater. The deep sandstone aquifers within the Bearpaw Formation which contribute significantly to the base flow in the river are not likely affected by surface mining. However, the shallow groundwater flow associated with springs along the river valley walls includes aquifers which contact the coal zone. Several of these springs have water quality characteristics which match those of mine spoil groundwater. Trudel (1988) estimated that the contribution of salt loads from these springs to the Battle River was of

Table 1.1 List of Industries for the Battle River Basin (List Compiled by the Standards and Approvals Division, Alberta Environment, 1990)

1.	Altex Resources Ltd. (Gas Plant), near Bittern Lake
2.	Border Paving Ltd. (Asphalt Plant), near Bittern Lake
3.	Burnco Rock Products Ltd. (Gravel Washing), near Ponoka
4.	Canadian Oil Reclamations (COR) Ltd. (Oil Reclaimer), near Lacombe
5.	County of Wetaskiwin No. 10 (Gravel Washing), near Wetaskiwin
6.	Domtar Ltd. (Wood Preserving), in Camrose
7.	Esso Resources Canada Limited (Gas Plant), near Bonnie Glen
8.	Lafarge Construction Materials (Gravel Washing), near Borle
9.	Mark Resources Inc. (Gas Plant), near Malmo
10.	North Canadian Oils Limited (Gas Plant), near Bruce
11.	Sceptre Resources Limited (Gas Plant), near Strome
12.	Kinsella Transit Mix Ltd. (Gravel Washing), near Kinsella
13.	Alberta Power Limited (Power Plant), near Forestburg on Battle River
14.	Amoco Canada Petroleum Company Ltd. (Gas Plant), near Provost
15.	Luscar Ltd. (Coal Processing), near Forestburg
16.	Manalta Coal Ltd. (Coal Processing), near Forestburg
17.	Rife Resources Ltd. (Gas Plant), near Ferintosh
18.	Francana Minerals (Chemical Plant), near Horseshoe Lake

minor importance.

Several intensive livestock operations (e.g., feedlots, hog or poultry farms) are located in close proximity to the Battle River or its tributaries. Although these operations do not have licenced discharges to the river it is likely that run-off from their grounds enters the river during spring melt and heavy rains. Pasture land and range land borders the Battle River in many locations and the river is a water source for the cattle. In most instances access to the water is uncontrolled and the passage of the animals contributes to bank slumping and erosion.

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2. METHOD DEVELOPMENT AND ANALYSIS OF FIELD SAMPLES FOR TRACE METALS IN SEDIMENT AND BIOTA

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2.1 INTRODUCTION

As one of the participants in Battle River Multi-Media Pilot Project, the Water Analysis and Research Branch (WA&RB), Chemistry Division, Alberta Environmental Centre, undertook the responsibility of developing laboratory techniques for determining trace level metals in sediment and biota. The design of this project required that these techniques focus on metals or metal species related to anthropogenic activity, rather than simply the total metals contained in these media. WA&RB was also responsible for analysing sediment and biota field samples using these techniques in order to assist staff from the Environmental Quality Monitoring Branch (EQMB) of Alberta Environment's Environmental Assessment Division in evaluating both the suitability of different media for metal pollution monitoring and the sampling techniques used in gathering these media.

Seven basic methods involving eleven metals, three analytical instruments, and two basic classes of matrices were developed. These methods were based on a brief literature survey and on the existing analytical techniques for the analysis of water and wastewater available at WA&RB. The performance of these methods was evaluated in terms of quality control samples analyzed in conjunction with the field samples. This evaluation indicated that the majority of methods developed were reasonably accurate and precise; a few methods require further development.

2.2 SOME CONSIDERATIONS IN THE SELECTION OF METHODS

As sediment and biota are complex matrices, not only are sample preparations rather involved, but the researcher is presented with many options regarding the particular species to be determined. The value of the data

compiled is ultimately determined by the choice of sample preparation, extraction/digestion[1], and analytical methodologies.

2.2.1 Metals of Interest

Pollution surveys of heavy metals in sediment and biota generally focus on those metals which have found common domestic and industrial uses. Those that have received the most attention are Cd, Cr, Cu, Hg, Pb, and Zn, with additional attention paid to As, Se, Ni, and V in areas where particularly heavy industrialization has occurred or where fossil fuels are produced or used extensively (Allan and Jackson 1978; Forstner and Wittmann 1981; Moore and Ramamoorthy 1984; Merriman 1987). Iron, Al, and Mn are generally not considered, particularly in sediment analysis, since they are major components of any sediment. Therefore, WA&RB staff geared their methods toward determining Cd, Cr, Cu, Ni, Pb, V, Zn, As, Se and Hg in the selected media.

Unique behaviour and/or superior detection techniques separate As, Se, and Hg from the rest of these elements. In the balance of this report, Cd, Cr, Cu, Ni, Pb, V, and Zn are regarded collectively as "heavy metals", As and Se as a second group, and Hg is regarded on its own.

2.2.2 Metal Species and Sample Fractions

Metals contained in sediment exist as a virtual continuum of species, ranging from extremely labile to extremely inert. Some investigators have operationally defined five "phases" of metals to be targeted in

[1]In this discussion, the term "extraction" is used to refer to acid treatments which leach a fraction other than the total amount of the analyte into solution. "Digestion", on the other hand, refers to treatments which mobilize all the analyte into solution.

extraction/digestion approaches (Tessier, Campbell and Bisson 1979; Calmano and Forstner 1983):

i)	Exchangeable:	weakly associated with the sediment through adsorption or ion-exchange mechanisms.
ii)	Carbonatic:	coprecipitated with or forming precipitate coatings on the calcitic/dolomitic phases in the sediment.
iii)	Reducible:	coprecipitated with or otherwise entrained in the naturally abundant iron and manganese oxyhydrates.
iv)	Organic/Sulphitic:	associated with humic materials, organisms, or other organic entities as well as metallic sulphides.
v)	Residual:	entrained in the silicate matrix of deposited rock and mineral matter.

Metals of anthropogenic origin are present almost exclusively as non-residual species (fractions i-iv above), so pollution assessment should focus on these phases particularly.

Another consideration in sediment analysis is that metal concentration is highly dependent on particle size. Generally speaking, more metals are associated with smaller sediment particles than with larger ones. To compensate for the influence of particle size on metal content, Forstner and Salomons (1980) advocate using only the sieved < 63 μm particle fraction of a sediment sample for metals analysis. Agemian and Chau (1976), on the other hand, propose using the < 180 μm fraction, citing Hawkes and Webb's (1962) findings that this fraction yields the greatest contrast between anomalous and background results.

Such species/size considerations in sediment analysis have some parallels in biota analysis. Though routine monitoring protocols usually call for determining total metals in a given tissue, the particular tissue or body part chosen for analysis can influence the amount of metal found. Mussels, for example, are known to concentrate more metals in their soft tissues than in their shells (Jordao and Nickless 1989), while fish accumulate more in their organs

than muscle (Moore and Ramamoorthy 1984). The age/size of an organism can also influence metal content, in that the older/larger the organism is, the more metal it tends to have accumulated (Forstner and Wittmann 1981). In practice, however, the size of organisms studied is dictated by what is available at the sample site, which in turn dictates whether the whole body or specific body parts are analyzed.

2.2.3 Extraction/Digestion Procedures for Sediment Analysis

For purposes of pollution assessment, measurement of total metal content in a sediment is less informative than the measurement of species fractions, operationally defined by the extracts used to isolate them. Total metal analysis, by definition, requires the breakdown of mineral matter in the sediment, and this fraction has little to do with metals of anthropogenic origin. Extractions which leave the residual phase essentially intact are therefore preferred. Unfortunately, no single extraction procedure has gained unanimous approval for routine use.

Some authors (Tessier, Campbell and Bisson 1979; Salomons and Forstner 1980; Calmano and Forstner 1983; McKee et al. 1989) advocate sequential extraction techniques, selectively leaching the different fractions with successively harsher reagents. However, these approaches are perhaps most informative in geochemical research or detailed pollution investigations, and are too tedious and labour intensive for routine implementation (Agemian and Chau 1976). Most authors therefore opt for extracting all non-residual metals in one step using either hot concentrated acids, or cold dilute acids or complexing agents.

Currently, hot acid extraction appears to be the method of choice. Many authors have chosen this analytical route, using HNO_3 or Aqua Regia (often supplemented with such reagents as H_2O_2) to extract metals from sediments (Ogugbuaja, Schwarzer and Wilson 1984; Harvey and Gil 1988; Pelletier and Canuel 1988; Peerzada and Rohoza 1989; Hall 1989; Harding and Goyette 1989; Sweeney and Naidu 1989; Windom et al. 1989). Still, Agemian and Chau (1976) have demonstrated that this approach leaches an undefined amount of metals from the mineral matter in the sediment, thereby giving a false indication of non-residual metals. Rather, these authors prescribe a room temperature extraction with 0.5N HCl, asserting that this reagent attacks organic as well as inorganic species while showing "no association with the type of rock forming the sediment". Indeed, this technique has been established as a standard method by Environment Canada (1979), and has been used in at least one recent study (Merriman 1987). Other proposed cold extraction reagents include 0.05N EDTA, 1N NH_2OH:HCl in 25% HOAc, 6M HCOOH, and 0.1N HNO_3 (Agemian and Chau 1976; Forstner and Wittmann 1981; Watanabe et al. 1982). There is therefore no 'correct' extraction method, and an investigator must choose a technique based on available instrumentation and the intended use of the data to be gathered.

Extraction/digestion procedures for the analysis of As, Se and Hg are somewhat different from those for the other metals. Procedures for these elements should not only extract inorganic matter, but should provide and maintain a strong oxidizing environment to decompose large amounts of organo-arsenic, organo-selenium and organo-mercury compounds and to retain the inorganic species of interest in solution (Agemian and Bedek 1980). Mixed acid extractions/digestions using such acid combinations as $HNO_3/HClO_4$, HNO_3/H_2SO_4, and $HNO_3/H_2SO_4/HClO_4$ are widely employed for this purpose.

It should be noted that such harsh extractions for As, Se and Hg in sediments are often treated as "total" digestions, even if the associated silicate matrix is not completely dissolved (cf. Vijan et al. 1976; Environment Canada 1979). This term is acceptable if these elements occur in the sediment exclusively as non-residual species, or if the amount left in residual forms after digestion is negligible. Although acid treatments which do not include HF do not dissolve siliceous matter, hot, fuming, concentrated mineral acids, such as HCl, $HClO_4$, and H_2SO_4, serve to dehydrate silicon species to silica, SiO_2 (Furman 1962; American Public Health Association 1989). This dehydration releases residual species associated with the silicon into solution, and analysis of this solution can give a good approximation of the total elemental concentrations. However, not all forms of silicon can be fully dehydrated in this way, so caution should be exercised in applying the term "total" to any sediment extraction/digestion scheme that does not include HF digestion.

2.2.4 Digestion Procedures for Biota Analysis

Digestion of biota for metals analysis is straightforward in that the determination of total metals in the selected tissue is generally desired. Such methods should allow for complete destruction of associated organic matter, leaving a clean solution matrix. Normally, relatively vigorous mixed acid digestions, such as HNO_3/H_2SO_4, $HNO_3/H_2SO_4/H_2O_2$, and $HNO_3/H_2SO_4/HClO_4$ are employed (Environment Canada 1981; Alberta Environmental Centre 1987). Care must be taken to avoid charring the organic matter when using H_2SO_4, however, since this creates a reducing environment which promotes loss of Se and Hg (Environment Canada 1981; Alberta Environmental Centre 1987).

2.2.5 Summary

Including biota and sediment in a pollution impact study requires making specific choices regarding the phases and species of metals to be examined and the selection of analytical techniques. These decisions are probably more difficult for sediment than for biota, since the phase boundaries in a sediment are poorly defined and there are no universally acceptable standard methods for attacking these phases. Whatever the approach taken, it is imperative that the data be qualified in terms of the fraction of the whole sample analyzed and in terms of the extraction/digestion procedure used.

2.3 EXPERIMENTAL

As noted earlier (Section 2.2.1), the metals originally targeted for analysis were Cd, Cr, Cu, Ni, Pb, V, Zn, As, Se and Hg. Determinations of Cd and Pb in biota, however, were not carried out due to poor precision and recoveries shown in preliminary investigations. Also, an additional parameter, Co, is cited with sediment results. This metal is not generally considered a pollutant, but is included here to possibly serve as a 'reference' element against which to assess the levels of the targeted metals. The selection of this particular element was quite arbitrary: Co data was available from the simultaneous ICP-AES used, and was present in all samples at low but measurable levels. Cobalt was particularly well behaved, showing precision and recovery generally as good as the best behaved target elements, and was treated as a target element in all steps of data processing.

2.3.1 Sample Preparation

Sample preparation includes splitting, and/or homogenizing, and/or drying a sample, yielding a material that is to be sub-sampled for extraction or digestion. The procedures applied to the samples analyzed in this study are summarized in Table 2.1.

Table 2.1 Summary of Sample Preparation

Sample		Description
Sediments		- Wet samples were split into two portions by coning and quartering. - One portion was reserved for Hg and moisture analysis, and was stored frozen. - The other portion was freeze-dried and sieved through 20- and 80-mesh stainless steel sieves; the portion passing through 80-mesh was reserved for the remaining analyses, and was stored at room temperature
Biota		
(1) Benthic Invertebrates	Amphipoda, Sphaeriidae, Gastropoda, Chironomidae, Simuliidae	- Samples were crushed and mixed in a porcelain mortar and pestle.
	Hirudinea, Unionidae	- Samples were chopped with a teflon spatula and then mixed in a porcelain mortar and pestle.
	Tubificidae	- Very small samples were received: no preparation was attempted.
(2) Fish		- Soft-frozen muscle tissue samples were chopped with the sharp edge of a 1"x1"x(1/4)" glass plate.
(3) Macrophytes		- Samples were split into two portions. - One portion was set aside for Hg and moisture analysis. - The other portion was freeze-dried and crushed in a porcelain mortar and pestle, with crushing facilitated by freezing the sample with a small amount of liquid nitrogen; this portion was reserved for the remaining analyses.

Notes:
1. All samples were received frozen and stored likewise. When ready for preparation, they were thawed at 4°C.
2. Unless stated, prepared samples were stored frozen until ready for analysis, at which time they were thawed at 4°C and allowed to warm to room temperature before being sub-sampled.

Note that the preparation of sediment is adopted from Environment Canada's method "Non-Residual Metals in Sediments" (Environment Canada 1979); preparations for biota are based on existing WA&RB methods for fish analysis (Alberta Environmental Centre 1987).

2.3.2 Extraction/Digestion Procedures

Standards were carried through the same extraction/digestion procedures as the samples.

For biota analysis, digestion procedures were adopted from existing digestion procedures for Analysis of "Heavy Metals" in Fish, Analysis of As and Se in Fish, and Analysis of Hg in Fish used in WA&RB (Alberta Environmental Centre 1987). These procedures are summarized in Table 2.2.

For sediment analysis, both the 0.5N HCl extraction, adopted from Environment Canada's method "Non-Residual Metals in Sediments" (Environment Canada 1979) and the Aqua Regia extraction (Kimbrough and Wakakuwa 1989; Alberta Environmental Centre 1987) were selected for the analysis of "heavy metals". Digestion procedures for the analysis of As, Se and Hg in sediments, however, were adapted from corresponding procedures for fish analysis used at WA&RB. Thus, they were similar to those used in biota analysis. These procedures are summarized in Table 2.3. It is important to bear in mind that all sediment extractions, except Hg, were conducted on the < 80-mesh (ie. < 180 μm) fraction of freeze-dried sediment; Hg analysis was performed on the whole, wet sediment.

2.3.3 Analytical Techniques and Systems

The analytical techniques and systems used for biota and sediment analysis are briefly described in Tables 2.4 and 2.5, respectively. These

Table 2.2 Summary of Digestion Procedures for Biota Analysis

Parameters	Description
"Heavy Metals" (Cu, Cr, Ni, V, Zn)	1. Weigh 5 g wet invertebrates or fish, or 1 g freeze-dried plant material into a 100-mL Kjeldahl flask. 2. Add 10 mL concentrated HNO_3 and 2 mL concentrated H_2SO_4 and allow the solution to sit several hours. 3. Heat gradually on a Labconco manifold until sample chars. 4. Let cool slightly, and add 50% H_2O_2 dropwise until the solution clears. 5. Repeat steps 3 and 4 until charring no longer occurs, and SO_3 fumes evolve. 6. Cool, add 10 mL water and 5 mL concentrated HCl, and dilute to volume in a 50-mL volumetric flask.
As & Se	1. Dispense 2 g wet invertebrates or fish, or 0.4 g freeze-dried plant material into a 100-mL Kjeldahl flask. 2. Add 5 mL concentrated HNO_3 and 3 mL concentrated H_2SO_4 and allow the solution to sit for several hours. 3. Heat gradually on a Labconco heating manifold, taking care that no charring occurs; add small amounts of concentrated HNO_3 whenever red-brown NO_2 fumes disappear in order to maintain oxidizing conditions. 4. Stop heating when SO_3 fumes evolve. 5. Cool, add 8 mL 25% $HClO_4$, and continue digestion until white fumes evolve. 6. Cool, add 10 mL 1+1 HCl and dilute to volume in a 50-mL volumetric flask.
Hg	1. Dispense 0.4 g wet biota into a 100-mL Kjeldahl flask. 2. Add 2.5 mL concentrated HNO_3 and 5 mL concentrated H_2SO_4 and allow the solution to sit for several hours. 3. Heat gradually on a Labconco manifold, taking care to avoid charring. 4. Stop heating when SO_3 fumes evolve. 5. Cool, add 5 mL water, 0.8 mL of 3% $K_2Cr_2O_7$/(1+1)HNO_3 preservative, and dilute to volume in a 50-mL volumetric flask.
Note: When storage is needed, the extracted sample is transferred to a 125-mL polypropylene screw-cap bottle.	

methods are basically those used at WA&RB for routine analysis of water and wastewater, with such minor modifications as preparing "heavy metals" standards in 0.5N HCl to match the 0.5N HCl extraction. Refer to WA&RB 's methods manual (Alberta Environmental Centre 1987) for details.

Table 2.3 Summary of Extraction/Digestion Procedures for Sediment Analysis

Parameters	Description
"Heavy Metals" (Cd, Co, Cu, Cr, Pb, Ni, V, Zn)	0.5N HCl Extraction at Room Temperature 1. Dispense 4 g freeze-dried, < 80-mesh sediment into a 125-mL polypropylene screw-cap bottle. 2. Add 40 mL 0.5N HCl and shake the solution on a table shaker overnight (16 hours). 3. Allow the solution to settle approximately 1 hour before analysis.
	Aqua Regia Extraction 1. Dispense 1 g freeze-dried, < 80-mesh sediment into a 100-mL Kjeldahl flask. 2. Add 15 mL concentrated HCl and 5 mL concentrated HNO_3 (i.e. 20 mL Aqua Regia) and boil the solution to a volume of less than 5 mL on a Labconco heating manifold. 3. Cool, add 5 mL concentrated HCl, transfer to a 50-mL volumetric flask, and dilute to volume.
As & Se	1. Dispense 1 g freeze-dried, < 80-mesh sediment, into a 100-mL Kjeldahl flask. 2. Add 5 mL concentrated HNO_3 and 3 mL concentrated H_2SO_4 and allow the solution to sit for several hours. 3. Heat gradually on a Labconco heating manifold, taking care that no charring occurs; add small amounts of concentrated HNO_3 whenever red-brown NO_2 fumes disappear to maintain oxidizing conditions. 4. Stop heating when SO_3 fumes evolve. 5. Cool, add 8 mL 25% $HClO_4$, and continue digestion until white fumes evolve. 6. Cool, add 10 mL 1+1 HCl and dilute to volume in a 50-mL volumetric flask.
Hg	1. Weigh an amount of wet sediment corresponding to 1 g dry weight into a 100-mL Kjeldahl flask. 2. Add 2.5 mL concentrated HNO_3 and 5 mL concentrated H_2SO_4 and allow the solution to sit for several hours. 3. Heat gradually on a Labconco manifold, taking care to avoid charring. 4. Stop heating when SO_3 fumes evolve. 5. Cool, add 5 mL water, 0.8 mL of 3% $K_2Cr_2O_7$/(1+1)HNO_3 preservative, and dilute to volume in a 50-mL volumetric flask.
Note: When storage is needed, the extracted sample is transferred to a 125-mL polypropylene screw-cap bottle.	

2.3.4 Measurement of Detection Limits

At the outset of this project, detection limits were not available for all methods. The detection limit of an analyte can be derived from replicate measurements on a material of similar matrix to the samples tested, and containing the analyte at low levels; such a detection limit is referred to as a Method Detection Limit (MDL), since variances due to all steps of the method

Table 2.4 Summary of Methods for Biota Analysis

Parameters			"Heavy Metals" (Cr, Cu, Ni, V, Zn)	As & Se	Hg	Moisture
Sample Preparation	Analysis Basis	Fauna	Wet	Wet	Wet	Wet
		Flora	Dry	Dry	Wet	Wet
	Sample Fraction		Whole	Whole	Whole	Whole
Extraction/ Digestion	Sample Weight	Fauna	5 g	2 g	0.4 g	1 g
		Flora	1 g	1 g	0.4 g	1 g
	Final Volume		50 mL	50 mL	50 mL	
	Acids		10% HNO_3, 2% H_2SO_4, 50% H_2O_2	5% HNO_3, 3% H_2SO_4, 2% $HClO_4$	2.5% HNO_3, 5% H_2SO_4	
Major Acids in Final Solution of Samples and Standards			10% HCl	10% HCl	1% HNO_3, 0.06% $K_2Cr_2O_7$	
Analytical Technique*			ICP-AES	Automated HGQFAAS	Automated CVAAS	Dry sample at 105°C for 16 hrs
Reagents Used in On-line Reaction/Digestion			none	1% $NaBH_4$ in 0.3% KOH, 1+1 HCl	Conc. H_2SO_4, 10% $SnCl_2$ in 10% HCl, 4% $K_2S_2O_8$	

* Analytical Technique Abbreviations:
ICP-AES = Inductively Coupled Plasma - Atomic Emission Spectroscopy
HGQFAAS = Hydride Generation Quartz Furnace Atomic Absorption Spectroscopy
CVAAS = Cold Vapour Atomic Absorption Spectroscopy

are reflected in the final value (cf. American Public Health Association 1989; Analytical Methods Committee 1987). Where such a material is not available, other approaches to obtaining the detection limit need to be considered.

In this study, wherever a suitable low level material was available or could be prepared, MDL's were determined using the approach outlined above. Where such a material was not available, detection limits were estimated, based on aqueous MDL's used routinely at WA&RB. These estimated limits were calculated as the aqueous limits (mg/L) multiplied by the final digest volume (L) and divided by the nominal sample weight (kg); as an example, given that the aqueous

Table 2.5 Summary of Methods for Sediment Analysis

Parameters		"Heavy Metals" (Cd, Co, Cr, Cu, Pb, Ni, V, Zn)		As & Se	Hg	Moisture	Loss on Ignition
		0.5N HCl Extraction	Aqua Regia Extraction				
Sample Preparation	Analysis Basis	Dry	Dry	Dry	Wet	Wet	Dry
	Sample Fraction	< 80-mesh	< 80-mesh	< 80-mesh	Whole	Whole	< 80-mesh
Extraction/ Digestion	Sample Weight	4 g	1 g	1 g	1 g	1 g	5 g
	Final Volume	40 mL	50 mL	50 mL	50 mL		
	Acids	0.5N HCl	Aqua Regia	5% HNO_3, 3% H_2SO_4, 2% $HClO_4$	2.5% HNO_3, 5% H_2SO_4		
Major Acids in Final Samples and Standards		0.5N HCl	10% HCl, 5-10% HNO_3	10% HCl	1% HNO_3, 0.06% $K_2Cr_2O_7$		
Analytical Technique*		ICP-AES	ICP-AES	Automated HGQFAAS	Automated CVAAS	Dry sample at 105°C for 16 hrs	Dry sample at 105°C for 16 hrs and then ignite at 550°C for 2 hrs
Reagents Used in On-line Reaction/Digestion		none	none	1% $NaBH_4$ in 0.3% KOH, 1+1 HCl	Conc. H_2SO_4, 10% $SnCl_2$ in 10% HCl, 4% $K_2S_2O_8$		

* see Table 2.4 for Analytical Technique abbreviations.

detection limit for Arsenic is 0.0008 mg/L, taking 2 g sample per 50 mL digest volume would yield a detection limit estimate of 0.02 mg/kg. An implicit assumption made with this estimate is that the matrix contributes a negligible variance over and above that contributed by aqueous samples. Of course, it is desirable to have MDL's determined for all parameters, but without suitable materials to determine these, the estimates cited above should provide reasonable approximations regarding the lower analytical limits of the methods used.

2.3.5 Quality Control Samples

The quality control (QC) samples used included certified reference materials (CRM's), in-house reference materials (IRM's), spiked samples, and duplicates, the latter two randomly selected from the field samples. Data from these were processed according to the existing QC protocol at WA&RB (Dieken, Habib and Kovacevich 1988).

Certified reference materials (CRM's) used in this study were obtained from the United States National Institute of Standards and Technology (NIST) (formerly the National Bureau of Standards (NBS))[2] and the United States Environmental Protection Agency (EPA). For biota analysis, NBS SRM[3] 1577a (Bovine Liver), NBS SRM 1573 (Tomato Leaves), NBS SRM 1575 (Pine Needles) and EPA Trace Metals in Fish were used. For sediment analysis, NBS SRM 1646 (Estuarine Sediment) and NBS SRM 2704 (Buffalo River Sediment) were used. Since all these CRM's were dry materials, in cases where wet samples were analyzed, the amount of CRM taken for analysis was calculated based on a typical moisture for the particular sample type. For example, a typical moisture content in fish muscle is 78%, and with 5 g wet weight required for heavy metal analysis, the aliquot of CRM for this digestion would be 5 g * ((100% - 78%) / 100%) = 1.1 g. Where dry samples were analyzed, an amount of CRM equal to the required sample aliquot was used.

Two sediment in-house reference materials (IRM's), QCA and QCB, were prepared from samples leftover from the analysis of the first batch of field samples received. These samples were combined in appropriate proportions to

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[2]Standards purchased from NIST were developed when that agency was known as NBS. These materials are therefore referred to as "NBS" standards in the balance of this report.

[3]The abbreviation "SRM" stands for "Standard Reference Material", which is how NIST refers to their own CRM's.

yield Cu concentrations of roughly 75% (QCA) and 25% (QCB) of the highest sample concentration observed in the first batch of samples. QCA and QCB were run as a pair with each batch of samples.

Spikes and duplicates were used to evaluate the accuracy and precision of the methods, respectively. In evaluating the accuracy, it was assumed that an analyte spike is chemically indistinguishable from the analyte contained in the sample.

A set of QC samples was included with each batch of field samples. These consisted of at least one certified reference material, at least two each of duplicates and spiked samples selected from the field samples, and, for all sediment batches except the first, two in-house reference materials. Data from these were compiled separately from the field samples and were submitted to statistical appraisal (Lucyk et al. 1992).

Note that Hg spike data cannot be regarded as reliable. It was found by supplementary investigations conducted after these samples were analyzed that the manner in which the spiking was performed may have caused loss during digestion. These losses would have only been reflected in the spiked samples, not in the unspiked samples, so this does not affect any of the other results. Data for spiked Hg samples should therefore be regarded as suspect, and are not considered in any discussions presented here.

2.3.6 Analysis of Field Samples

Sample analyses were run in batches which roughly corresponded to sample shipments received by WA&RB.

For some biota samples, not all the parameters could be determined due to a limited amount of sample. When such cases occurred, analyses were given the

priority "heavy metals" > Hg > As & Se > moisture, and were conducted in sequence until the sample was exhausted. It is indicated in the applicable tables where such shortages occurred.

2.3.7 Expression and Calculation of Results

Results for biota analyses are expressed as "total" elemental concentrations, since the biota digestions destroy all organic matter in the sample. Conversely, since the heavy metals extractions on sediment target only the non-residual metals, these were termed "extractable". It is not uncommon, however, for extraction/digestion procedures similar to those selected here for As, Se, and Hg in sediment to be treated as "total" sediment digestions, even though the siliceous material is not dissolved (Vijan et al. 1976; Environment Canada 1979). Presumably, it is assumed that such treatments are harsh enough to destroy the sample's silicate matrix, restructuring it to SiO_2 and releasing all entrained elements into solution, as mentioned in Section 2.2.3 above. No tests were undertaken to confirm or disprove whether this occurs for the samples under consideration in the present study. Results for As, Se, and Hg in sediments should therefore be regarded as representing "extractable" metals.

The calculations used for the reported results are listed in Table 2.6. Slight differences exist in the way in which field samples and QC samples are reported. For the field samples (Tables 2.19 - 2.25), concentrations which were measurable at levels between 1/3 of the detection limit and the detection limit are reported in parentheses, while those falling below 1/3 the detection limit are reported as less than the detection limit. For QC samples (Tables 2.8 - 2.18), concentrations which were measurable at levels between 1/3 of the detection limit and the detection limit are reported in parentheses, just as the

Table 2.6 Summary of Calculations Used

Moisture	$\text{Moisture}(\%) = 100 * \frac{\text{Wet wt.(g)} - \text{Dry wt.(g)}}{\text{Wet wt.(g)}}$
Loss on Ignition (LOI)	$\text{LOI}(\%) = 100 * \frac{\text{Dried wt.(g)} - \text{Ignited wt.(g)}}{\text{Initial sample wt. (g)}}$
Metals	$\text{Concentration (mg/kg)} = \text{Solution Concentration (mg/L)} * \frac{\text{Solution Vol.(mL)}}{\text{Sample Wt.(g)}}$
Conversion of Concentration from Wet to Dry Basis	$\text{Dry Basis (mg/kg)} = \text{Wet Basis (mg/kg)} * \frac{100\ \%}{100\% - \text{Moisture}\ \%}$

results for field samples are, but those below 1/3 the detection limit are reported as less than 1/3 the detection limit and are enclosed in parentheses as well. This was done to reduce the influence of 'less than' values on subsequent calculations. Where a 'less than' value was included in a calculation, it was assigned the value 1/3 the detection limit for the particular parameter and the calculation was performed as usual. Calculated data which is based on at least one such 'less than' result is preceded with a "#" flag in the tables.

Although the Hg in sediment extraction and most biota digestions were conducted on wet samples, results are expressed on the dry basis as well, in order that they may be compared more readily with guideline and literature data. Where applicable, the conversion was performed according to the formula given in Table 2.6. In cases where the wet basis result was less than the detection limit, the dry basis result is expressed as less than the dry basis value

calculated from the corresponding wet basis detection limit. Due to varying moisture contents, this approach sometimes yielded different calculated 'dry basis detection limits' for samples which were otherwise similar.

Data calculated from results of QC samples were not rounded, in order to avoid truncating significant but small numbers during the course of calculations. Apparent outlying data were submitted to Dixon's Q-test (Skoog and West 1983; Rorabacher 1991) to decide if they should be rejected. Rejected data are preceded with "r" flags in the tables, and are not included in subsequent calculations.

2.4 RESULTS AND DISCUSSION

2.4.1 Detection Limits

Detection limits cited in this report are given in Table 2.7. Unparenthesized limits given in Table 2.7 are MDL's, directly determined using the approach outlined in Section 2.3.4, whereas parenthesized limits are estimates based on the aqueous MDL's used routinely at WA&RB. It should be noted that detection limits cited here depend not only on the sensitivity and the noise level of the method, but also on the amount of sample used and on the final volume of the extraction/digestion solution. For this reason, that information is also included in Table 2.7. Moreover, when reported 'less than' values on the dry basis are derived from measurements on wet samples, these 'dry basis detection limits' are related to the moisture level of the wet sample, as noted in Section 2.3.7, above. Therefore, a fair comparison between detection limits of similar methods can only be made when these 'concentration' or 'dilution' factors have been considered.

2.4.2 Performance of Biota Analysis

Recoveries of metals from Certified Reference Materials are given in Tables 2.8 - 2.11. For EPA Trace Metals in Fish, these recoveries were excellent. For NBS SRM 1577a (Bovine Liver), NBS SRM 1573 (Tomato Leaves), and NBS SRM 1575 (Pine Needles), recoveries were generally good, ranging from 73 - 111%. Only V and Se in NBS 1577a showed low recoveries of 35% and 23%, respectively. Failure of V in NBS 1577a might be explained by the fact that the certified concentration (0.099 mg/kg) is at the level of the detection limit (on a dry basis) of the method (see Table 2.7), where precision is poor. Failure of Se in NBS 1577a, in which the Se level is well above the detection limit, suggests that the method for Se should be considered suspect.

Spike recoveries are given in Table 2.12. Considering the diversity and complexity of the matrices handled in biota analyses, recoveries of most metals are reasonably good. The average recoveries for each metal, calculated for all species tested, ranged from 75% to 125% (not shown in Table 2.12).

Method precision can be evaluated from standard deviations of measurements on the certified reference materials and from relative errors in duplicate analyses (Table 2.13). For the majority of duplicate analyses, the relative error is less than 30%. The high relative error of Se duplicates is consistent with the high standard deviation of Se in the analysis of CRM's. This poor precision of Se is probably inherent in the method itself.

Table 2.7 Detection Limits

Sample Parameter(s)	Analysis Basis	Sample Fraction Analyzed	Nominal Sample Weight (g)	Digest/ Extract Volume (mL)	Detection Limit (mg/kg)											
					Moisture	LOI	Cu	Zn	Cd	Pb	Co	Ni	Cr	V	As	Se	Hg
Sediment																	
Moisture	Wet	Whole	1		(0.1)												
Loss on Ignition	Dry	< 80-mesh	5			0.03											
"Heavy Metals" (0.5N HCl)	Dry	< 80-mesh	4	40			0.07	0.12	0.07	0.11	0.05	0.07	0.06	0.06			
"Heavy Metals" (Aqua Regia)	Dry	< 80-mesh	1	50			0.11	0.3	0.7	4	0.3	0.8	0.6	1.2			
As & Se	Dry	< 80-mesh	1	50											0.4	0.006	
Hg	Wet	Whole	1s	50													0.002
Invertebrates and Fish																	
Moisture	Wet	Whole	1		(0.1)												
"Heavy Metals"	Wet	Whole	5	50			0.2	3				0.2	0.08	0.03			
As & Se	Wet	Whole	2	50											0.007	0.07	
Hg	Wet	Whole	0.4	50													0.008
Macrophytes																	
Moisture	Wet	Whole	1		(0.1)												
"Heavy Metals"	Dry	Whole	1	50			(0.4)	(0.2)				(0.6)	(0.4)	(0.1)			
As & Se	Dry	Whole	0.4	50											(0.10)	(0.05)	
Hg	Wet	Whole	1	50													(0.01)
Routine Aqueous MDL's at WA&RB (mg/L)							0.008	0.004	0.002	0.010	0.001	0.012	0.008	0.002	0.0008	0.0004	0.0002

s -- Weight of Wet Sample Corresponding to 1 g Dry Weight

Note: Values in parentheses indicate estimated detection limits. For metals, estimates are based on Routine Aqueous detection limits used at WA&RB, multiplied by the ratio of the final solution volume to the nominal sample weight: ie. D.L.[est](mg/kg) = {D.L.[aq](mg/L)} * {vol(mL)/wt(g)}.

Table 2.8 Analysis of EPA Trace Metals in Fish

		Total Metals Concentrations -- As Determined (mg/kg)							
		Cu	Zn	Ni	Cr	V	As	Se	Hg
Certified Values									
Mean = $\bar{X}$ & S_c		2.21 ± 0.64	43.6 ± 4.05	0.54 ± 0.28	0.58 ± 0.38		2.43 ± 0.79	0.37 ± 0.19	2.52 ± 0.64
Observed Values	1	2.0	40	0.5	0.53	1.03	1.740		2.712
	2	2.0	39	0.5	0.54	1.17			
	3	2.1	41	0.8	0.65	1.13			3.047
	4	2.5	41	0.3	0.96	1.73			
n		4	4	4	4	4			2
Mean = $\bar{X}$ & S_o		2.15 ± 0.238	40.25 ± 0.957	0.525 ± 0.206	0.67 ± 0.201	1.265 ± 0.316			2.8795 ± 0.2369
RSD (%)		11	2	39	30	25			8
Recovery (%)		97	92	97	116				114

Table 2.9 Analysis of NBS SRM 1577a (Bovine Liver)

		Total Metals Concentrations -- As Determined (mg/kg)							
		Cu	Zn	Ni	Cr	V	As	Se	Hg
Certified Values									
Mean = $\bar{X}$ & S_c		158 ± 7	123 ± 8			0.099 ± 0.008	0.047 ± 0.006	0.71 ± 0.07	0.004 ± 0.002
Observed Values	1	151.4	116	< (0.1)	0.36	< (0.01)	0.044	(0.02)	(0.004)
	2	139.5	111	0.2	0.72	0.07	0.032	(0.02)	< (0.003)
	3	137.7	117	0.5	0.83	0.05	0.036	0.45	(0.004)
	4	142.3	117	(0.1)	0.40	< (0.01)			
n		4	4	# 4	4	# 4	3	3	# 3
Mean = $\bar{X}$ & S_o		142.7 ± 6.085	115.3 ± 2.872	# 0.225 ± 0.189	0.578 ± 0.233	# 0.035 ± 0.03	0.0373 ± 0.0061	0.163 ± 0.248	# 0.0037 ± 0.0006
RSD (%)		4	2	# 84	40	# 86	16	152	# 16
Recovery (%)		90	94			# 35	79	23	# 92

Table 2.10 Analysis of NBS SRM 1573 (Tomato Leaves)

		Total Metals Concentrations -- As Determined (mg/kg)							
		Cu	Zn	Ni	Cr	V	As	Se	Hg
Certified Values									
Mean = $\bar{X}$ & S_c		11 ± 1	62 ± 6		4.5 ± 0.5		0.27 ± 0.05		[0.1]
Observed Values	1	9.4	58.8	0.9	3.1	1.41	0.34	(0.03)	0.094
	2	8.9	61.5	1.6	3.1	1.12	0.26	(0.03)	0.061
	3	9.1	58.0	1.4	3.6	1.56			
n		3	3	3	3	3	2	2	2
Mean = $\bar{X}$ & S_o		9.133 ± 0.252	59.43 ± 1.834	1.3 ± 0.361	3.267 ± 0.289	1.363 ± 0.224	0.3 ± 0.0566	0.03 ± 0	0.0775 ± 0.0233
RSD (%)		3	3	28	9	16	19	0	30
Recovery (%)		83	96		73		111		78

Table 2.11 Analysis of NBS SRM 1575 (Pine Needles)

		Total Metals Concentrations -- As Determined (mg/kg)							
		Cu	Zn	Ni	Cr	V	As	Se	Hg
Certified Values									
Mean = $\bar{X}$ & S_c		3.0 ± 0.3		[3.5]	2.6 ± 0.2		0.21 ± 0.04		0.15 ± 0.05
Observed Values	1								0.097
	2								0.120
	3	2.7	64.4	1.5	2.1	(0.04)	0.24	(0.05)	0.121
	4	2.9	70.0	2.4	2.3	0.14	0.18	(0.03)	0.121
	5	2.8	66.6	2.6	2.4	0.22			
n		3	3	3	3	3	2	2	4
Mean = $\bar{X}$ & S_o		2.8 ± 0.1	67 ± 2.821	2.167 ± 0.586	2.267 ± 0.153	0.133 ± 0.09	0.21 ± 0.0424	0.04 ± 0.014	0.1148 ± 0.0118
RSD (%)		4	4	27	7	68	20	35	10
Recovery (%)		93		62	87		100		76

Table 2.12 Analysis of Biota Spikes

Sample Type	Pair Number (i)	Total Metals Concentrations -- As Determined (mg/kg) Cu	Zn	Ni	Cr	V	As	Se	Hg
Observed Values (y_i, y_{ik}, where "k" designates spike)									
Invertebrate	1	10.2	15	(0.2)	0.39	0.48			
Invertebrate	1k	11.1	18	2.6	2.77	2.66			
Invertebrate	2						1.630		0.015
Invertebrate	2k						10.500		0.271
Invertebrate	3	2.3	8	1.9	1.53	0.84	2.900		< (0.003)
Invertebrate	3k	3.7	12	3.5	2.13	2.74	10.700		0.230
Invertebrate	4	3.4	10	1.0	0.59	1.11	2.410		< (0.003)
Invertebrate	4k	5.6	13	3.4	1.60	3.25	11.200		0.186
Invertebrate	5	8.8	10	0.5	0.17	0.41	0.155	0.10	(0.006)
Invertebrate	5k	9.3	14	2.5	2.21	2.34	0.239	0.18	0.090
Invertebrate	6	1.0	47	0.4	0.41	(0.01)	0.365	(0.03)	0.011
Invertebrate	6k	2.4	69	2.0	2.08	1.46	0.648	0.19	0.080
Fish	7	0.5	4 <	(0.1)	0.10	(0.02)	0.007	(0.02)	0.112
Fish	7k	2.3	6	1.8	1.88	1.93	0.063	0.08	0.056
Fish	8	(0.2)	6 <	(0.1)	0.11	(0.02)	0.010	< (0.02)	0.103
Fish	8k	1.9	7	1.7	1.73	1.80	0.055	0.11	0.127
Macrophyte	9	1.8	10.8	3.3	0.5	1.56	1.19	0.09	< (0.003)
Macrophyte	9k	11.2	22.9	13.5	10.4	12.25	1.55	0.31	0.087
Macrophyte	10	6.6	18.6	9.2	4.5	9.90	2.22	0.30	< (0.003)
Macrophyte	10k	14.9	29.3	18.9	14.3	19.98	2.35	0.50	0.049
Designed Spike Values (K_i)									
Invertebrate	1	2.0	2	2.0	2.00	2.00			
Invertebrate	2						10.031		0.237
Invertebrate	3	2.0	2	2.0	1.99	1.99	9.344		0.241
Invertebrate	4	2.0	2	2.0	2.00	2.00	9.849		0.224
Invertebrate	5	1.9	2	1.9	1.91	1.91	0.165	0.17	0.092
Invertebrate	6	1.8	2	1.8	1.77	1.77	0.129	0.13	0.080
Fish	7	1.8	2	1.8	1.83	1.83	0.047	0.05	0.101
Fish	8	2.0	2	2.0	1.96	1.96	0.044	0.04	0.096
Macrophyte	9	10.0	10.0	10.0	10.0	9.95	0.25	0.25	0.094
Macrophyte	10	10.0	10.0	10.0	10.0	10.00	0.25	0.25	0.093
Recovery % (R_i = 100% * ((y_{ik} - y_i)/K_i))									
Invertebrate	1	45	150	120	119	109			
Invertebrate	2						88		108
Invertebrate	3	70	200	80	30	95	83	#	94
Invertebrate	4	110	150	120	61	107	89	#	82
Invertebrate	5	26	200	105	107	101	51	47	91
Invertebrate	6	78	1100	89	94	82	219	123	86
Fish	7	100	100 #	94	97	104	119	120	-55
Fish	8	85	50 #	80	83	91	102 #	225	25
Macrophyte	9	94	121	102	99	107	144	88 #	89
Macrophyte	10	83	107	97	98	101	52	80 #	49

Table 2.13 Analysis of Biota Duplicates

Sample Type	Pair Number (i)	Total Metals Concentrations -- As Determined (mg/kg) Cu	Zn	Ni	Cr	V	As	Se	Hg
Observed Values									
Invertebrate	1	8.0	14	0.2	0.42	0.44	1.350		0.014
Invertebrate	1	8.9	11	(0.2)	0.39	0.42	1.200		0.014
Invertebrate	2						1.860		0.013
Invertebrate	2						1.990		(0.006)
Invertebrate	3	8.6	14	0.3	0.56	0.95			
Invertebrate	3	9.1	14	0.3	0.56	0.98			
Invertebrate	4						1.020		< (0.003)
Invertebrate	4						1.020		< (0.003)
Invertebrate	5	9.7	11 <	(0.1)	(0.08)	0.16	0.497	(0.06)	0.009
Invertebrate	5	11.0	10 <	(0.1)	0.09	0.19	0.678	0.11	0.012
Invertebrate	6	4.4	8	0.6	(0.06)	0.24	0.268	0.11	(0.004)
Invertebrate	6	3.7	9	0.8	0.27	0.44	0.139	0.10	(0.004)
Fish	7	0.6	3 <	(0.1)	0.10	(0.02)	< (0.002)	(0.06)	0.246
Fish	7	0.5	3 <	(0.1)	0.10	(0.01)	< (0.002)	0.11	0.231
Fish	8	(0.2)	5 <	(0.1)	0.11	(0.02)	0.019	0.08	0.106
Fish	8	0.2	4 <	(0.1)	0.11	(0.02)	< (0.002)	(0.06)	0.098
Macrophyte	9	1.9	8.3	1.8	0.7	0.11	0.94	0.09	0.058
Macrophyte	9	1.9	8.6	1.3	0.5	0.12	1.01	0.10	0.049
Macrophyte	10	5.7	20.6	7.8	3.6	7.99	3.54	0.32	< (0.003)
Macrophyte	10	6.3	21.1	7.6	3.7	8.34	4.99	0.31	< (0.003)
Relative Error (%) = 100 * (|Duplicate1 - Duplicate2|/(Average of Duplicates))									
Invertebrate	1	11	24	0	7	5	12		0
Invertebrate	2						7		74
Invertebrate	3	6	0	0	0	3			
Invertebrate	4						0	#	0
Invertebrate	5	13	10 #	0	12	17	31	59	29
Invertebrate	6	17	12	29	127	59	63	10	0
Fish	7	18	0 #	0	0	67 #	0	59	6
Fish	8	0	22 #	0	0	0 #	162	29	8
Macrophyte	9	0	4	32	33	9	7	11	17
Macrophyte	10	10	2	3	3	4	34	3 #	0

2.4.3 Performance of Sediment Analysis

Since the present sediment methods only determine the concentration of metals which are acid extractable, their accuracy cannot be evaluated from measurements on CRM's, for which total concentrations of each parameter have been certified. Thus, assessment of accuracy depends mainly on the recovery study of spiked samples. Nevertheless, certified reference materials NBS SRM 1646 (Estuarine Sediment) and NBS SRM 2704 (Buffalo River Sediment) were analyzed to gain information on the extracted concentration relative to the total concentration of each measured parameter. Precision was determined from the CRM's, IRM's and duplicates.

2.4.3.1 Recoveries from Spiked Samples

Table 2.14 summarizes the recoveries from spiked sediments. Recoveries of "heavy metals" spikes from Aqua Regia extracts ranged from 89 - 104% for Cu, 50 - 140% for Zn, 96 - 106% for Cd, 40 - 110% for Pb, 86 - 110% for Co, 75 - 117% for Ni, 76 - 125% for Cr and 60 - 124% for V. Recoveries of "heavy metals" from 0.5N HCl extracts were generally low, ranging from 68 - 126% for Cu, 50 - 96% for Zn, 82 - 94% for Cd, 72 - 91% for Pb, 74 - 93% for Co, 63 - 88% for Ni, 63 - 89% for Cr and 74 - 93% for V. This discrepancy between the efficiencies of the two extractants may be explained by the different mechanisms through which metals are leached into solution.

Acid extractions can release metals from sediment by either competing with active sites in the sediment for associated metals, or by destroying these sites altogether. Through normal chemical equilibria, metals so released into solution will distribute between the aqueous solution and whatever competitive sites in the sediment are not destroyed. An analyte spike added to the

extractant/sediment system will participate in whatever equilibria exist. If a significant portion of highly competitive sites remains intact, the amount of spike recovered will be lower than the amount added. Thus, since only the metals in the aqueous phase are measured, the more destructive an extractant is toward a sediment, the more efficient it will appear to be.

In 0.5N HCl, one would expect that metals associated with most carbonates, sulphides, and oxyhydrates would undergo significant destructive extraction, while those associated with organic ligands and those held on exchangeable sites would be more prone to competitive extraction. If these latter species predominate, and their extractions are incomplete, spike recovery will be low, due to extractant/sediment partitioning. In contrast, Aqua Regia is expected to be more destructive toward exchangeable and organically bound metals, so spike recovery from Aqua Regia is more likely to be high. Low spike recovery from 0.5N HCl, therefore, does not translate into poor performance of this extractant; rather, this simply reveals the different mechanisms under which such extractions operate.

The extraction used in the As and Se approach, like the Aqua Regia method, is a destructive extraction. The spike recovery of As was reasonably good, but that for Se was poor (Table 2.14). Assuming that the behaviour of the spike reflects similar behaviour of Se in the sample, the accuracy of the Se method is called into question. Such under-recovery would occur if the digestion conditions had not been maintained sufficiently oxidizing, or if all the Se had not been converted to Se(IV) prior to hydride generation, as mentioned earlier. Until these possibilities are investigated further, results for Se should be considered suspect.

2.4.3.2 Results from Certified Reference Materials

Results for certified reference materials NBS SRM 1646 (Estuarine Sediment) and NBS SRM 2704 (Buffalo River Sediment) are presented in Tables 2.15 and 2.16. It is to be expected that most metals will have low recoveries, since only extractable metals were determined with the present methods, while the total concentration of each metal was certified. These tables are included to offer information on the portion of extracted concentration relative to the total concentration for each measured parameter.

It is expected that 0.5N HCl, being a milder extractant than Aqua Regia, would extract less metal. This is indeed what was observed, with recoveries of most "heavy metals" from CRM's being lower for 0.5N HCl extraction (10 - 49%) than corresponding recoveries from Aqua Regia (49 - 85%). The notable exceptions to this are Cd and Pb, for which recoveries by the two extractants are more comparable; in fact, in one case -- Pb from NBS 1646 -- 0.5N HCl recovers more metal.

A more rigorous statistical evaluation (Lucyk et al. 1992) indicates that Aqua Regia extracted essentially all the Cu from both CRM's. This suggests that the bulk of this metal contained in these CRM's exists in a readily extractable form. Whether this can be extended to sediments in general, though, is uncertain.

Data observed for As, Se, and Hg in these sediments is probably more informative than that for extractable heavy metals, since the methods used target a larger fraction of the total metals, as discussed above. Arsenic data show good recovery of this metal by the method under consideration. On the other hand, Hg data for NBS 1646 indicates that recovery of this metal at the level contained in this material may not be complete. Selenium is not a certified

parameter in either of these CRM's, but the low recovery observed relative to the "non-certified" values provided by NBS, does suggest poor recovery of Se by the method used.

2.4.3.3 Precision of Sediment Analysis

The standard deviations $S_{r,IRM}$, S_A and S_B, derived from paired analysis of in-house reference materials, QCA and QCB, and the standard deviation $S_{r,Dup}$, derived from the analysis of duplicates, are summarized in Table 2.17. The original data of $S_{r,Dup}$ is given in Table 2.18, while the original IRM data is given elsewhere (Lucyk et al. 1992).

Table 2.17 shows that, for concentrations significantly above the detection limits, relative standard deviations (RSD's) based on the average of observed values are generally below 10%, indicating good precision. The exception to this is the between-run standard deviation in low level Se. The apparent poor precision of 0.5N HCl extraction of Cd and Aqua Regia extraction of Cd and Pb arises from the low levels of these elements observed in the QC samples: for concentrations near the detection limit, RSD is expected to be high.

Table 2.14 Analysis of Sediment Spikes

Pair Number (i)	0.5N HCl Extractable Metal Concentrations (mg/kg)								Aqua Regia Extractable Metal Concentrations (mg/kg)								Other Metals (mg/kg)		
	Cu	Zn	Cd	Pb	Co	Ni	Cr	V	Cu	Zn	Cd	Pb	Co	Ni	Cr	V	As	Se	Hg
Observed Values (y_i, y_{ik}, where "k" designates spike)																			
1	1.97	7.83	(0.06)	2.43	1.76	4.39	3.35	1.43	2.71	21.5	< (0.2)	(3)	3.7	8.6	11.1	12.5			0.004
1k	3.40	9.54	1.84	4.19	3.56	6.02	4.69	3.23	13.15	35.5	10.8	14	14.7	20.3	23.6	24.9			0.120
2																			0.010
2k																			0.096
3	1.39	8.07	(0.02)	2.31	2.01	3.19	0.53	1.52	2.59	23.2	< (0.2)	(2)	4.2	8.0	7.5	12.3			
3k	3.84	9.24	1.75	4.04	3.51	4.49	2.08	3.13	12.58	33.9	10.4	12	14.4	18.2	16.9	22.1			
4	1.16	8.34	< (0.02)	2.44	2.05	3.30	0.57	1.61	2.09	19.5	< (0.2)	(3)	3.6	6.8	6.6	12.5	3.5	0.013	< (0.001)
4k	3.54	10.73	2.26	4.71	4.34	5.51	2.80	3.96	12.06	30.8	10.4	12	13.7	16.5	16.5	22.0	9.1	0.040	0.052
5	6.08	27.49	0.13	3.74	3.09	7.55	3.17	5.92	9.69	53.8	< (0.2) <	(1)	7.4	18.5	22.9	25.5	3.4	0.228	0.007
5k	8.07	28.76	2.18	5.55	4.94	9.12	4.94	7.81	18.63	58.9	9.9	10	16.1	26.1	30.6	34.4	8.8	0.215	0.033
6	10.45	30.36	0.12	6.84	3.69	7.33	1.74	6.44	14.32	58.4	< (0.2)	(3)	7.0	14.7	14.8	25.9	3.8	0.168	0.016
6k	12.14	31.61	2.28	8.99	5.57	8.92	3.30	8.43	23.38	65.1	9.9	12	15.9	23.5	22.4	31.7	6.4	0.073	0.018
7	2.28	11.36	(0.02)	3.08	2.97	18.98	23.31	2.66	3.36	24.0	< (0.2)	(2)	4.7	29.9	52.5	12.6	4.1	0.041	0.007
7k	4.43	13.32	2.32	5.34	5.09	16.88	17.79	4.90	13.72	35.3	9.9	12	15.3	44.7	72.0	24.4	10.3	0.053	0.046
8	1.83	10.05	< (0.02)	2.68	2.39	4.54	1.45	2.03	2.92	23.6	< (0.2)	(2)	4.4	8.5	8.2	14.5	4.0	0.032	0.007
8k	3.99	12.00	2.37	6.87	4.55	6.58	3.35	4.20	12.54	34.0	9.9	10	14.0	18.6	18.8	25.5	8.8	0.106	0.017
9	8.54	37.34	0.21	3.14	3.54	22.41	23.95	7.59	14.64	68.1	(0.2) <	(1)	8.2	36.3	55.5	28.5	3.4	0.548	0.015
9k	10.50	39.07	2.51	5.63	5.75	19.01	12.86	9.43	24.30	77.2	10.1	5	17.6	45.9	64.7	39.0	8.0	0.606	0.032
Designed Spike Values (K_i)																			
1	1.94	1.94	1.94	1.94	1.94	1.94	1.94	1.94	10.00	10.0	10.0	10	10.0	10.0	10.0	10.0			0.156
2																			0.186
3	1.98	1.98	1.98	1.98	1.98	1.98	1.98	1.98	9.94	9.9	9.9	10	9.9	9.9	9.9	9.9			
4	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50	9.99	10.0	10.0	10	10.0	10.0	10.0	10.0	5.1	0.101	0.066
5	2.51	2.51	2.51	2.51	2.51	2.51	2.51	2.51	10.08	10.1	10.1	10	10.1	10.1	10.1	10.1	5.0	0.098	0.051
6	2.49	2.49	2.49	2.49	2.49	2.49	2.49	2.49	9.73	9.7	9.7	10	9.7	9.7	9.7	9.7	4.6	0.090	0.046
7	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50	9.95	9.9	9.9	10	9.9	9.9	9.9	9.9	4.9	0.095	0.065
8	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50	9.81	9.8	9.8	10	9.8	9.8	9.8	9.8	5.1	0.099	0.069
9	2.49	2.49	2.49	2.49	2.49	2.49	2.49	2.49	10.00	10.0	10.0	10	10.0	10.0	10.0	10.0	5.1	0.100	0.039
Recovery % (R_i = 100% * $((y_{ik} - y_i)/K_i)$)																			
1	74	88	92	91	93	84	69	93	104	140 #	106	110	110	117	125	124			74
2																			46
3	124	59	87	87	76	66	78	81	101	108 #	103	100	103	103	95	99			
4	95	96 #	90	91	92	88	89	94	100	113 #	102	90	101	97	99	95	110	27 #	77
5	79	51	82	72	74	63	71	75	89	50 #	96 #	90	86	75	76	88	108	-13	51
6	68	50	87	86	76	64	63	80	93	69 #	100	90	92	91	78	60	57	-106	4
7	86	78	92	90	85	-84	-221	90	104	114 #	98	100	107	149	197	119	127	13	60
8	86	78 #	94	168	86	82	76	87	98	106 #	99	80	98	103	108	112	94	75	14
9	79	69	92	100	89	-137	-445	74	97	91	99 #	40	94	96	92	105	90	58	44

Table 2.15 Analysis of NBS SRM 1646 (Estuarine Sediment)

		0.5M HCl Extractable Metal Concentrations (mg/kg)								Aqua Regia Extractable Metal Concentrations (mg/kg)								Other Metals (mg/kg)		
		Cu	Zn	Cd	Pb	Co	Ni	Cr	V	Cu	Zn	Cd	Pb	Co	Ni	Cr	V	As	Se	Hg
Certified Values																				
Mean = X_c		18	138	0.36	28.2	10.5	32	76	94	18	138	0.36	28.2	10.5	32	76	94	11.6	[0.6]	0.063
Std Dev S_c		3	6	0.07	1.8	1.3	3	3	1	3	6	0.07	1.8	1.3	3	3	1	1.3		0.012
Observed Values	1	5.94	62.26	0.29	13.49	1.97	4.59	5.76	15.90	15.63	114.6	(0.2)	12	8.0	20.6	36.5	44.9			0.047
	2									14.41	105.9	(0.3)	(1)	8.3	19.3	37.9	49.2			
	3	6.38	64.34	0.24	14.02	2.49	5.83	7.12	18.28	15.14	110.8	(0.4)	11	7.9	19.9	36.2	45.5	9.3	0.174	0.026
	4	6.67	71.04	0.23	15.02	2.89	6.94	8.40	19.98	15.49	119.0	(0.2)	8	8.6	22.8	37.0	47.6	9.4	0.384	0.031
	5	6.95	72.18	0.29	15.14	2.86	6.78	8.05	19.79	15.64	114.4	(0.3)	6	8.7	22.7	37.6	47.9	13.2	0.366	0.036
n		4	4	4	4	4	4	4	4	5	5	5	5	5	5	5	5	3	3	4
Mean = X_k		6.485	67.455	0.263	14.418	2.5525	6.035	7.3325	18.49	15.26	112.9	0.28	7.6	8.3	21.06	37.04	47.02	10.63	0.308	0.035
Std Dev S_k		0.431	4.8945	0.032	0.7965	0.4288	1.081	1.1793	1.885	0.517	4.893	0.084	4.393	0.354	1.61	0.716	1.78	2.223	0.1164	0.009
RSD (%)		7	7	12	6	17	18	16	10	3	4	30	58	4	8	2	4	21	38	26
Recovery (%)		36	49	73	51	24	19	10	20	85	82	78	27	79	66	49	50	92	51	56

Table 2.16. Analysis of NBS SRM 2704 (Buffalo River Sediment)

		0.5M HCl Extractable Metal Concentrations (mg/kg)								Aqua Regia Extractable Metal Concentrations (mg/kg)								Other Metals (mg/kg)		
		Cu	Zn	Cd	Pb	Co	Ni	Cr	V	Cu	Zn	Cd	Pb	Co	Ni	Cr	V	As	Se	Hg
Certified Values																				
Mean = X_c		98.6	438	3.45	161	14.0	44.1	135	95	98.6	438	3.45	161	14.0	44.1	135	95	23.4	[1.1]	1.44
Std Dev S_c		5.0	12	0.22	17	0.6	3.0	5	4	5.0	12	0.22	17	0.6	3.0	5	4	0.8		0.07
Observed Values	1	59.08	190.20	2.47	82.00	2.23	6.01	21.08	3.86	95.78	398.3	3.2	139	10.4	31.1	74.2	23.1			1.390
	2									85.74	371.1	2.9	115	10.3	29.7	74.3	25.8			
	3	63.31	237.01	2.36	98.54	2.86	7.91	24.45	5.00	91.60	374.4	3.2	132	10.2	30.1	73.5	24.4	20.0	0.180	0.657
	4	66.62	265.03	2.74	114.77	3.30	9.36	27.88	5.65	93.30	412.2	2.8	148	11.2	34.4	76.7	26.3	20.7	0.515	1.417
	5	67.68	262.60	2.83	115.14	3.29	9.18	27.78	5.17	96.15	405.9	2.8	144	11.5	35.0	76.5	26.2	24.0	0.741	1.176
n		4	4	4	4	4	4	4	4	5	5	5	5	5	5	5	5	3	3	4
Mean = X_k		64.12	238.71	2.6	102.61	2.92	8.115	25.297	4.92	92.51	392.4	2.98	135.6	10.72	32.06	75.04	25.16	21.57	0.4287	1.16
Std Dev S_k		3.872	34.735	0.221	15.771	0.5037	1.545	3.232	0.758	4.22	18.62	0.205	12.97	0.589	2.472	1.459	1.379	2.136	0.2823	0.3522
RSD (%)		6	15	9	15	17	19	13	15	5	5	7	10	5	8	2	5	10	59	30
Recovery (%)		65	54	75	64	21	18	19	5	94	90	86	84	77	73	56	26	92	44	81

Table 2.17 Precision Estimates of Sediment Analyses

	LOI (wt %)	Metal Concentrations (mg/kg) Cu	Zn	Cd	Pb	Co	Ni	Cr	V	As	Se	Hg
0.5N HCl Extraction												
MDL		0.07	0.12	0.07	0.11	0.05	0.07	0.06	0.06			
Between-run Standard Deviation:												
n_A		3	3	3	3	3	3	3	3			
S_A		0.32	2.1192	0.047	0.4477	0.1955	0.541	0.2122	0.364			
X_A		9.963	33.96	0.153	5.8567	3.8133	8.753	2.9333	7.193			
RSD (%)		3	6	31	8	5	6	7	5			
n_B		3	3	# 3	3	3	3	3	3			
S_B		0.068	0.1041	# 0.023	0.2871	0.0115	0.056	0.0208	0.101			
X_B		2.747	11.483	# 0.033	3.1467	2.3333	4.24	0.9167	2.487			
RSD (%)		2	1	# 69	9	0	1	2	4			
Within-run Standard Deviation												
n_{IRM}		3	3	# 3	3	3	3	3	3			
$S_{r,IRM}$		0.265	1.4647	# 0.025	0.1321	0.1451	0.363	0.1582	0.225			
X_{AB}		6.355	22.722	# 0.093	4.5017	3.0733	6.497	1.925	4.84			
RSD (%)		4	6	# 27	3	5	6	8	5			
n_{Dup}		8	8	# 8	8	8	8	8	8			
$S_{r,Dup}$		0.1	0.4545	# 0.037	0.1075	0.0671	0.225	0.1157	0.123			
X_{Dup}		8.391	27.041	# 0.143	5.6194	3.5537	7.828	2.3562	5.634			
RSD (%)		1	2	# 26	2	2	3	5	2			
Aqua Regia Extraction												
MDL		0.11	0.3	0.7	4	0.3	0.8	0.6	1.2			
Between-run Standard Deviation:												
n_A		5	5	# 5	# 5	5	5	5	5			
S_A		0.676	3.3864	# 0.13	# 1.3416	0.497	1.72	1.4363	2.371			
X_A		14.42	63.26	# 0.28	# 1.6	7.48	18.72	19.76	26.32			
RSD (%)		5	5	# 47	# 84	7	9	7	9			
n_B		5	5	# 5	# 5	5	5	5	5			
S_B		0.278	1.0597	# 0	# 0.4472	0.1871	0.63	0.6189	1.644			
X_B		4.132	26.44	# 0.2	# 1.2	4.3	8.58	7.64	14.76			
RSD (%)		7	4	# 0	# 37	4	7	8	11			
Within-run Standard Deviation:												
n_{IRM}		5	5	# 5	# 5	5	5	5	5			
$S_{r,IRM}$		0.36	1.8718	# 0.092	# 0.6325	0.2757	0.846	0.9892	1.633			
X_{AB}		9.274	44.85	# 0.24	# 1.4	5.89	13.65	13.7	20.54			
RSD (%)		4	4	# 38	# 45	5	6	7	8			
n_{Dup}		7	8	# 8	8	8	8	8	8			
$S_{r,Dup}$		0.291	1.6304	# 0.056	# 1.2247	0.1803	0.502	1.3811	1.912			
X_{Dup}		12.74	54.681	# 0.219	# 3	7.15	18.57	19.2	22.73			
RSD (%)		2	3	# 26	# 41	3	3	7	8			
Other Methods												
MDL	0.03									0.4	0.006	0.002
Between-run Standard Deviation:												
n_A	2									3	2	1
S_A	0.0071									0.416	0.0057	NA
X_A	7.805									4.567	0.34	0.042
RSD (%)	0									9	2	NA
n_B	3									3	3	1
S_B	0.0058									0.503	0.0116	NA
X_B	1.1333									3.733	0.0463	0.015
RSD (%)	1									13	25	NA
Within-run Standard Deviation:												
n_{IRM}	2									3	2	1
$S_{r,IRM}$	0									0.216	0.0145	NA
X_{AB}	4.4692									4.15	0.1932	0.0285
RSD (%)	0									5	8	NA
n_{Dup}	6									6	6	8
$S_{r,Dup}$	0.1637									0.187	0.0115	0.0023
X_{Dup}	4.8675									5.357	0.2216	0.0126
RSD (%)	3									3	5	18

Table 2.18 Analysis of Sediment Duplicates

Pair Number (i)	Loss on Ign. (wt %)	Total Moisture (wt %)	0.5M HCl Extractable Metal Concentrations (mg/kg)								Aqua Regia Extractable Metal Concentrations (mg/kg)								Other Metals (mg/kg)		
			Cu	Zn	Cd	Pb	Co	Ni	Cr	V	Cu	Zn	Cd	Pb	Co	Ni	Cr	V	As	Se	Hg
Observed Values																					
1			10.38	31.28	0.18	5.91	3.08	6.01	2.13	5.93	r 23.13	69.6	(0.2)	7	6.9	17.8	16.4	21.9			0.015
1			10.67	32.36	0.27	6.18	3.13	6.19	2.25	6.08	r 17.10	73.7	(0.2)	6	7.4	18.2	18.7	25.5			0.024
2											9.51	51.5	(0.2)	(2)	6.6	18.1	16.9	18.8			
2											9.70	53.0	< (0.2)	(2)	6.8	18.3	17.8	20.3			
3			9.56	28.54	0.13	6.57	3.34	5.83	2.05	5.41											
3			9.50	28.76	0.19	6.53	3.39	5.94	2.09	5.49											
4																					0.002
4																					(0.002)
5			6.49	28.95	0.12	3.53	3.28	8.64	3.49	6.46	9.25	47.3	< (0.2)	(4)	6.6	17.1	19.9	23.5	3.3	0.248	0.009
5			6.57	28.10	0.12	3.50	3.10	8.10	3.18	6.16	9.87	51.5	(0.4) <	(1)	6.8	18.0	20.2	22.2	3.0	0.254	0.008
6		23.2																			
6		24.1																			
7		54.9																			
7		55.6																			
8			1.49	9.74	< (0.02)	3.11	2.27	3.68	0.70	1.92	2.54	22.8	< (0.2)	(2)	4.0	7.7	7.7	13.9	3.6	0.022	(0.002)
8			1.43	9.07	< (0.02)	2.92	2.22	3.54	0.61	1.77	2.46	22.3	< (0.2)	(4)	3.9	6.6	6.3	12.4	4.0	0.017	0.002
9	4.76																				
9	4.94																				
10	1.09		3.07	13.82	(0.05)	3.49	3.17	5.92	1.43	2.90	4.94	32.0	< (0.2)	(2)	5.4	11.8	8.5	14.6	r 10.6		0.010
10	1.46		3.01	13.37	< (0.02)	3.62	3.13	5.65	1.35	2.93	4.71	31.6	< (0.2)	(2)	5.7	11.6	9.1	16.4	r 4.8		0.010
11	5.73		13.87	39.34	0.20	9.83	3.82	8.54	1.95	8.08	19.59	71.4	< (0.2)	(4)	8.2	18.0	17.4	30.7	3.7	0.163	0.025
11	5.86		14.09	39.20	0.23	9.83	3.82	8.63	1.97	8.13	19.88	72.3	< (0.2)	5	8.2	17.7	14.6	25.3	3.5	0.159	0.023
12	0.93																				
12	1.08																				
13	11.51	63.7	8.72	37.69	0.23	3.48	3.53	9.77	3.73	7.60	13.60	65.7	(0.3) <	(1)	8.1	21.0	21.6	27.0	4.4	0.584	0.012
13	11.68	63.7	8.65	37.08	0.21	3.57	3.37	9.18	3.47	7.29	14.23	66.7	< (0.2) <	(1)	8.1	21.5	22.7	28.6	4.2	0.585	0.012
14																			5.3	0.106	
14																			5.3	0.132	
15	4.83	40.5	13.41	27.39	0.10	8.81	6.07	14.74	3.72	7.01	21.89	72.7	< (0.2)	(1)	11.0	37.5	46.5	32.3	9.8	0.209	0.023
15	4.54	40.5	13.34	27.96	0.19	9.03	6.14	14.89	3.58	6.99	21.42	70.8	< (0.2)	(4)	10.7	36.3	42.9	30.2	9.5	0.180	0.023
Relative Error (%) = 100 * (|Duplicate1 - Duplicate2|/(Average of Duplicates))																					
1			3	3	40	4	2	3	5	2		6	0	15	7	2	13	15			46
2											2	3 #	0	0	3	1	5	8			
3			1	1	38	1	1	2	2	1											
4																					0
5			1	3	0	1	6	6	9	5	6	9 #	67 #	120	3	5	1	6	10	2	12
6		4																			
7		1																			
8			4	7 #	0	6	2	4	14	8	3	2 #	0	67	3	15	20	11	11	26	0
9	4																				0
10	29		2	3 #	86	4	1	5	6	1	5	1 #	0	0	5	2	7	12			0
11	2		2	0	14	0	0	1	1	1	1	1 #	0	22	0	2	17	19	6	2	8
12	15																				
13	1	0	1	2	9	3	5	6	7	4	5	2 #	40 #	0	0	2	5	6	5	0	0
14																			0	22	
15	6	0	1	2	62	2	1	1	4	0	2	3 #	0	120	3	3	8	7	3	15	0

2.4.4 Results of Field Samples Analysis

Results of analysis of biota samples are listed in Tables 2.19 - 2.21, and those of sediment samples in Tables 2.22 - 2.25. Some important notes regarding these results are as follows:

- The As and Se analytical system was poorly behaved at the time of analysis of May - June/89 samples. Therefore, no results are reported for As and Se in sediment, and Se in invertebrates for these sample sets.

- The first batch of invertebrates (sampled June/89) was rinsed with distilled water before further preparation; the second batch (sampled September/89) was not.

- During the drying of August/89 Camrose Creek in-site variability sediment samples, the freeze-drier developed a vacuum leak which apparently decreased the efficiency of the unit. The resulting dried samples consisted of hard lumps rather than the free-flowing granules observed under normal freeze-drying conditions. These lumps were lightly crushed by hand in a porcelain mortar and pestle prior to passage through the 80-mesh sieve. As this operation was not comparable to the routine sample treatment, weight percentages for the < 80-mesh fraction of these samples is not given. Rather, the label "NA" is given them in Table 2.23.

For the sake of completeness, all data, regardless of the performance of the method used to collect it, is presented here. This includes data for Hg in sediment and Se in both sediment and biota: QC sample appraisal has cast doubt on the methods used for these parameters (cf. Sections 2.4.2 and 2.4.3). Data for Hg in sediment and Se in both matrixes should therefore be regarded with caution.

A detailed discussion of all results, with respect to their implications for pollution monitoring in the Battle River, has been formulated by EQMB staff, and is given in Section 3 of this report.

Table 2.19 Total Metals in Benthic Invertebrates

Sample Date	Sample Site	Taxa	Total Moisture (wt %)	Total Metal Concentrations (mg/kg) — Wet Basis - As Determined								Dry Basis - As Calculated							
				Cu	Zn	Ni	Cr	V	As	Se	Hg	Cu	Zn	Ni	Cr	V	As	Se	Hg
Invertebrates Sampled June, 1989																			
Jun 20/89	Hwy 611	Amphipoda	89.4	8.0	14	0.2	0.42	0.44	1.350		0.014	75	130	2	4.0	4.2	12.74		0.13
Jun 21/89	Hwy 53	Amphipoda	89.5	10.2	15	(0.2)	0.39	0.48	1.240		0.014	97	140	(2)	3.7	4.6	11.81		0.13
Jun 22/89	Camrose Creek	Amphipoda	87.7	8.6	14	0.3	0.56	0.95	1.630		0.015	70	110	2	4.6	7.7	13.25		0.12
Jun 23/89	Hwy 872	Amphipoda	86.7	11.0	16	0.5	0.67	1.13	1.710		(0.005)	83	120	4	5.0	8.5	12.86		(0.04)
Jun 28/89	Unwin	Amphipoda	87.6	10.0	15	0.3	0.39	0.71	1.020		< 0.008	81	120	2	3.1	5.7	8.23		< 0.06
Jun 28/89	Battleford	Amphipoda	85.2	13.0	17	0.5	0.70	1.11	1.390		0.008	88	110	3	4.7	7.5	9.39		0.05
Jun 22/89	Camrose Creek	Chironomidae	*	3.0	15	1.9	2.98	5.66	**		**	*	*	*	*	*	*		*
Jun 20/89	Hwy 611	Hirudinea	88.5	2.1	42	(0.2)	0.22	0.16	1.610		(0.007)	18	370	(2)	1.9	1.4	14.00		(0.06)
Jun 21/89	Hwy 53	Hirudinea	91.7	3.5	36	< 0.2	0.11	0.11	1.710		(0.007)	42	430	< 2	1.3	1.3	20.60		(0.08)
Jun 22/89	Camrose Creek	Hirudinea	91.1	1.5	27	(0.1)	0.08	0.10	1.740		0.026	17	300	(1)	0.9	1.1	19.55		0.29
Jun 23/89	Hwy 872	Hirudinea	90.3	2.9	45	0.2	(0.07)	0.09	1.880		< 0.008	30	460	2	(0.7)	0.9	19.38		< 0.08
Jun 20/89	Hwy 611	Simuliidae	89.2	3.0	30	1.4	2.51	2.64	2.560		0.014	28	280	13	23.2	24.4	23.70		0.13
Jun 20/89	Hwy 611	Sphaeriidae	63.4	3.0	15	0.5	1.10	1.38	1.550		0.014	8.2	41	1.4	3.0	3.77	4.23		0.04
Jun 21/89	Hwy 53	Sphaeriidae	55.2	3.1	16	0.4	0.44	0.79	1.860		0.013	6.9	36	0.9	1.0	1.76	4.15		0.03
Jun 23/89	Hwy 872	Sphaeriidae	43.4	2.3	8	1.9	1.53	0.84	2.900		< 0.008	4.1	14	3.4	2.7	1.48	5.12		< 0.01
Jun 28/89	Unwin	Sphaeriidae	42.3	2.9	10	0.6	0.30	0.60	0.800		< 0.008	5.0	17	1.0	0.5	1.04	1.39		< 0.01
Jun 28/89	Battleford	Sphaeriidae	41.4	3.4	10	1.0	0.59	1.11	2.410		< 0.008	5.8	17	1.7	1.0	1.89	4.11		< 0.01
Jun 22/89	Camrose Creek	Tubificidae	*	2.4	10	6.0	13.34	4.45	**		**	*	*	*	*	*	*		*
Jun 21/89	Hwy 53	Unionidae	88.0	0.8	32	< 0.2	0.35	(0.02)	1.790		0.025	7	270	< 2	2.9	(0.2)	14.92		0.21
Jun 23/89	Hwy 872	Unionidae	87.5	1.2	32	0.4	0.30	< 0.03	0.960		0.011	10	260	3	2.4	< 0.2	7.68		0.09
Jun 28/89	Battleford	Unionidae	*	1.5	41	0.4	0.42	0.13	0.800		< 0.008	*	*	*	*	*	*		*
Invertebrates Sampled September-October, 1989																			
Sep 26/89	Hwy 611	Amphipoda	87.2	9.7	11	< 0.2	(0.08)	0.16	0.497	(0.06)	0.009	76	90	< 2	(0.6)	1.2	3.88	(0.5)	0.07
Sep 27/89	Hwy 53	Amphipoda	85.7	9.6	11	< 0.2	(0.07)	0.14	0.140	0.13	(0.005)	67	80	< 1	(0.5)	1.0	0.98	0.9	(0.03)
Sep 28/89	Camrose Creek	Amphipoda	88.0	8.8	10	0.5	0.17	0.41	0.155	0.10	(0.006)	73	80	4	1.4	3.4	1.29	0.8	(0.05)
Sep 29/89	Hwy 872	Amphipoda	85.1	12.3	10	0.3	0.22	0.47	0.530	(0.02)	(0.004)	83	70	2	1.5	3.2	3.56	(0.1)	(0.03)
Oct 03/89	Unwin	Amphipoda	86.2	11.9	9	0.3	0.23	0.45	0.408	(0.03)	(0.006)	86	70	2	1.7	3.3	2.96	(0.2)	(0.04)
Oct 03/89	Battleford	Amphipoda	*	9.9	9	0.2	0.15	0.36	**	**	(0.005)	*	*	*	*	*	*	*	*
Oct 04/89	Battleford	Amphipoda	*	9.5	9	0.3	0.16	0.40	**	**	(0.004)	*	*	*	*	*	*	*	*
Sep 26/89	Hwy 611	Gastropoda	84.3	7.0	9	0.6	0.49	0.96	0.181	0.10	0.013	44.6	60	3.8	3.1	6.1	1.15	0.6	0.08
Sep 27/89	Hwy 53	Gastropoda	82.3	7.6	8	0.7	0.41	0.81	0.203	0.14	(0.004)	42.9	50	4.0	2.3	4.6	1.15	0.8	(0.02)
Sep 28/89	Camrose Creek	Gastropoda	80.5	14.4	11	1.2	0.63	1.40	0.510	(0.03)	0.018	73.8	60	6.2	3.2	7.2	2.62	(0.2)	0.09
Sep 28/89	Camrose Creek	Gastropoda	80.7	11.5	11	1.2	0.59	1.26	0.538	(0.02)	0.015	59.6	60	6.2	3.1	6.5	2.79	(0.1)	0.08
Sep 29/89	Hwy 872	Gastropoda	79.1	8.6	8	1.0	0.40	0.99	0.429	0.15	(0.004)	41.1	38	4.8	1.9	4.7	2.05	0.7	(0.02)
Sep 26/89	Hwy 611	Hirudinea	*	**	**	**	**	**	**	**	**	*	*	*	*	*	*	*	*
Sep 26/89	Hwy 611	Sphaeriidae	57.6	2.5	10	0.2	0.22	0.36	0.264	(0.07)	(0.004)	5.9	24	0.5	0.5	0.85	0.62	(0.2)	(0.01)
Sep 26/89	Hwy 53	Sphaeriidae	52.0	4.2	11	0.4	0.26	0.51	0.334	0.08	(0.005)	8.8	23	0.8	0.5	1.06	0.70	0.2	(0.01)
Sep 29/89	Hwy 872	Sphaeriidae	56.1	2.1	4	0.4	(0.03)	0.23	0.893	0.12	(0.004)	4.8	9	0.9	(0.1)	0.52	2.03	0.3	(0.01)
Oct 03/89	Unwin	Sphaeriidae	45.7	4.4	8	0.6	(0.06)	0.24	0.268	0.11	(0.004)	8.1	15	1.1	(0.1)	0.44	0.49	0.2	(0.01)
Oct 03/89	Battleford	Sphaeriidae	41.0	2.0	4	0.5	0.15	0.34	0.480	0.10	(0.004)	3.4	7	0.8	0.3	0.58	0.81	0.2	(0.01)
Sep 28/89	Camrose Creek	Tubificidae	*	2.2	19	1.0	1.76	3.40	**	**	**	*	*	*	*	*	*	*	*
Sep 29/89	Hwy 872	Unionidae	94.1	0.4	18	(0.2)	0.29	< 0.03	0.169	0.15	(0.007)	7	310	(3)	4.9	< 0.5	2.86	2.5	(0.12)
Sep 29/89	Hwy 872	Unionidae	93.4	0.7	17	0.7	0.22	0.06	0.191	0.18	0.009	11	260	11	3.3	0.9	2.89	2.7	0.14
Oct 03/89	Unwin	Unionidae	87.2	1.0	47	0.4	0.41	(0.01)	0.365	(0.03)	0.011	8	370	3	3.2	(0.1)	2.85	(0.2)	0.09
Oct 03/89	Unwin	Unionidae	86.3	0.8	15	0.2	0.17	0.11	0.384	0.30	0.010	6	110	2	1.2	0.8	2.80	2.2	0.07
Oct 04/89	Battleford	Unionidae	91.0	1.1	35	0.4	0.30	< 0.03	0.550	0.36	0.018	12	390	4	3.3	< 0.3	6.11	4.0	0.20
Oct 04/89	Battleford	Unionidae	90.7	0.9	39	0.4	0.21	< 0.03	0.080	0.18	0.011	10	420	4	2.3	< 0.3	0.86	1.9	0.12

Legend: * -- Insufficient sample for moisture analysis
** -- Insufficient sample for analysis

Table 2.20 Total Metals in Fish Sampled in November, 1989

Sample Date	Sample Site	Taxa	Total Moisture (wt %)	Total Metal Concentrations (mg/kg) — Wet Basis - As Determined								Dry Basis - As Calculated							
				Cu	Zn	Ni	Cr	V	As	Se	Hg	Cu	Zn	Ni	Cr	V	As	Se	Hg
Nov 1/89	Forestburg Res.	White Sucker	76.7	0.6	3 < 0.2		0.10	(0.02)	< 0.007	(0.06)	0.246	2.6	13 < 0.9		0.4	(0.09)	< 0.03	(0.3)	1.06
Nov 1/89	Forestburg Res.	White Sucker	79.2	0.4	4 < 0.2		0.15	(0.03)	< 0.007	(0.04)	0.169	1.9	19 < 1.0		0.7	(0.14)	< 0.03	(0.2)	0.81
Nov 1/89	Forestburg Res.	White Sucker	79.9	0.4	4 < 0.2		0.11	(0.02)	< 0.007	(0.06)	0.167	2.0	20 < 1.0		0.5	(0.10)	< 0.03	(0.3)	0.83
Nov 1/89	Forestburg Res.	White Sucker	77.4	0.5	4 < 0.2		0.10	(0.02)	0.007	(0.02)	0.112	2.2	18 < 0.9		0.4	(0.09)	0.03	(0.1)	0.50
Nov 1/89	Forestburg Res.	White Sucker	77.6	0.4	4 < 0.2		0.14	(0.02)	0.031	0.08	0.104	1.8	18 < 0.9		0.6	(0.09)	0.14	0.4	0.46
Nov 1/89	Forestburg Res.	Pike	78.0	0.2	4 < 0.2		0.12	(0.02)	< 0.007	(0.06)	0.219	0.9	18 < 0.9		0.5	(0.09)	< 0.03	(0.3)	1.00
Nov 1/89	Forestburg Res.	Pike	77.5	0.2	5 < 0.2		0.11	(0.03)	< 0.007	0.09	0.232	0.9	22 < 0.9		0.5	(0.13)	< 0.03	0.4	1.03
Nov 1/89	Forestburg Res.	Pike	78.3	0.2	5 < 0.2		0.12	(0.03)	< 0.007	0.08	0.341	0.9	23 < 0.9		0.6	(0.14)	< 0.03	0.4	1.57
Nov 1/89	Forestburg Res.	Pike	78.5	0.3	4 < 0.2		0.10	(0.03)	0.013	0.08	0.144	1.4	19 < 0.9		0.5	(0.14)	0.06	0.4	0.67
Nov 1/89	Forestburg Res.	Pike	76.7	0.3	4 < 0.2		0.10	(0.02)	0.023	(0.07)	0.225	1.3	17 < 0.9		0.4	(0.09)	0.10	(0.3)	0.97
Nov 1/89	Forestburg Res.	Pike	78.6	(0.2)	5 < 0.2		0.11	(0.02)	0.019	0.08	0.106	(0.9)	23 < 0.9		0.5	(0.09)	0.09	0.4	0.50
Nov 1/89	Forestburg Res.	Pike	78.5	(0.2)	6 < 0.2		0.11	(0.02)	0.010	< 0.07	0.103	(0.9)	28 < 0.9		0.5	(0.09)	0.05	< 0.3	0.48

Table 2.21 Total Metals in Macrophytes Sampled in August, 1989

Date Sampled	Sample Site	Taxa	Total Moisture (wt %)	Total Metal Concentrations (mg/kg) — Dry Basis - As Determined							Hg	
				Cu	Zn	Ni	Cr	V	As	Se	wet basis (as det'd)	dry basis (as calc'd)
Aug 01/89	Hwy 611	P.R. (S&L)	83.0	1.9	8.3	1.8	0.7	0.11	0.94	0.09	0.058	0.34
Aug 01/89	Hwy 53	P.R. (S&L)	85.2	2.6	17.1	1.8	1.2	1.28	0.95	0.09	< 0.010	< 0.07
Aug 02/89	Camrose Creek	P.R. (S&L)	84.3	1.8	10.8	3.3	0.5	1.56	1.19	0.09	< 0.010	< 0.06
Aug 02/89	Hwy 872	P.R. (S&L)	85.9	7.6	38.0	9.6	3.1	5.11	2.14	0.24	< 0.010	< 0.07
Aug 03/89	Unwin	P.R. (S&L)	81.3	5.7	20.6	7.8	3.6	7.99	3.54	0.32	< 0.010	< 0.05
Aug 03/89	Battleford	P.R. (S&L)	82.3	6.6	18.6	9.2	4.5	9.90	2.22	0.30	< 0.010	< 0.06
Aug 01/89	Hwy 611	P.R. (R)	91.0	14.0	59.6	16.5	30.2	43.05	7.74	0.53	(0.007)	(0.08)
Aug 01/89	Hwy 53	P.R. (R)	86.9	5.2	33.2	6.3	11.7	21.13	28.27	0.16	(0.004)	(0.03)
Aug 02/89	Camrose Creek	P.R. (R)	87.5	4.6	24.2	3.5	5.7	14.02	40.96	0.07	< 0.010	< 0.08
Aug 02/89	Hwy 872	P.R. (R)	88.2	8.4	38.3	9.3	12.2	31.56	243.19	0.17	< 0.010	< 0.08
Aug 03/89	Unwin	P.R. (R)	82.9	3.9	18.0	3.7	4.5	11.96	224.57	0.07	< 0.010	< 0.06
Aug 03/89	Battleford	P.R. (R)	*	14.9	32.1	8.3	9.6	18.75	**	**	**	*
Aug 01/89	Hwy 611	F.G.A.	92.5	9.7	42.7	7.7	8.6	11.22	1.69	0.21	< 0.010	< 0.13
Aug 01/89	Hwy 53	F.G.A.	91.6	2.8	19.5	2.3	3.8	6.28	1.34	0.09	< 0.010	< 0.12
Aug 02/89	Camrose Creek	F.G.A.	89.9	4.3	11.1	6.0	2.6	4.18	6.16	0.20	(0.005)	(0.05)
Aug 02/89	Hwy 872	F.G.A.	90.8	2.8	12.7	2.9	3.9	7.49	1.09	0.19	< 0.010	< 0.11
Aug 03/89	Unwin	F.G.A.	90.5	5.3	15.6	9.2	5.0	10.08	25.29	0.24	< 0.010	< 0.11

Legend:

* -- Insufficient sample for moisture analysis
** -- Insufficient sample for analysis

P.R. (S&L) = Potamogaeton richardsoni (Stems and Leaves)
P.R. (R) = Potamogaeton richardsoni (Roots)
F.G.A. = Filamentous Green Algae

Table 2.22 Routine Monitoring Sediments: Physical Parameters; Extractable Arsenic, Selenium, and Mercury

Date Sampled	Sample Site	Total Moisture (wt %)	Thru 80-mesh Fraction (wt %)	Loss on Ignition (wt %)	Metal Concentrations (mg/kg) As	Se	Hg wet basis	Hg dry basis
Bottom Sediments								
May 16/89	Hwy 611	41.3	66.7	8.81			0.010	0.017
May 16/89	Hwy 53	35.6	57.1	7.63			0.015	0.023
May 16/89	Camrose Creek	44.7	80.4	5.99			0.020	0.036
May 17/89	Hwy 872	17.0	26.4	2.22			0.006	0.007
May 17/89	Unwin	19.6	53.7	0.80			0.004	0.005
May 17/89	Battleford	14.4	22.5	1.16			< 0.002	< 0.002
Jun 20/89	Hwy 611	48.5	81.3	7.93			0.015	0.029
Jun 21/89	Hwy 53	19.3	10.1	6.69			0.010	0.012
Jun 22/89	Camrose Creek	44.1	61.9	5.75			0.016	0.029
Jun 23/89	Hwy 872	15.4	8.6	2.05			0.003	0.004
Jun 28/89	Unwin	19.3	17.5	0.81			0.002	0.002
Jun 28/89	Battleford	16.7	3.5	4.35			0.004	0.005
Jun 20/89	Battle Lake	45.6	96.0	3.55	3.6	0.108	0.006	0.011
Jun 21/89	Dried Meat Lake	67.8	55.0	10.09	4.2	0.211	0.012	0.037
Jun 23/89	Forestburg Res.	66.6	42.6	7.89	5.7	0.207	0.012	0.036
Aug 01/89	Hwy 611	57.4	71.7	7.51	3.3	0.248	0.009	0.021
Aug 01/89	Hwy 53	26.8	11.7	7.03	7.6	0.129	0.011	0.015
Aug 02/89	Camrose Creek	66.5	70.3	7.22	4.1	0.152	0.008	0.024
Aug 02/89	Hwy 872	23.2	15.4	1.97	6.1	0.059	0.004	0.005
Aug 03/89	Unwin	20.6	16.7	0.62	3.5	0.013	< 0.002	< 0.003
Aug 03/89	Battleford	18.5	3.2	2.78	10.8	0.061	< 0.002	< 0.002
Sep 26/89	Hwy 611	54.9	68.8	7.95	3.4	0.228	0.007	0.016
Sep 27/89	Hwy 53	29.2	14.2	7.43	8.3	0.139	0.018	0.025
Sep 28/89	Camrose Creek	70.8	66.6	7.66	4.3	0.157	0.008	0.027
Sep 29/89	Hwy 872	24.5	11.6	3.87	6.9	0.093	0.004	0.005
Oct 03/89	Unwin	20.6	24.5	0.76	3.6	0.022	(0.002)	(0.003)
Oct 03/89	Battleford	24.8	1.1	5.76	26.0	0.100	< 0.002	< 0.003
Feb 07/90	Hwy 611	63.7	83.4	11.51	4.4	0.584	0.012	0.033
Feb 06/90	Hwy 53	30.0	14.9	7.91	8.9	0.324	0.016	0.023
Feb 07/90	Camrose Creek	73.6	33.7	8.77	6.4	0.304	0.009	0.034
Feb 07/90	Hwy 872	25.0	6.3	3.92	11.7	0.173	0.005	0.007
Feb 08/90	Unwin	21.3	44.3	0.73	4.0	0.032	0.007	0.009
Feb 08/90	Battleford	21.5	29.3	2.37	5.3	0.106	0.006	0.008
Apr 23/90	Hwy 611	59.7	85.7	12.11	3.4	0.548	0.015	0.037
Apr 23/90	Camrose Creek	50.3	53.1	5.28	5.0	0.230	0.019	0.038
Apr 26/90	Unwin	22.9	81.6	0.57	3.2	0.025	0.004	0.005
Suspended Sediments								
Apr 23/90	Hwy 611	73.4	97.8	27.96	8.1	0.782	0.013	0.049
Apr 24/90	Camrose Creek	51.8	95.4	14.28	7.8	0.374	0.016	0.033
Apr 25/90	Unwin	40.5	82.4	4.83	9.8	0.209	0.023	0.039

Table 2.23 Surficial Replicate and Core Sediments: Physical Parameters; Extractable Arsenic, Selenium, and Mercury

Date Sampled	Sample Site		Total Moisture (wt %)	Thru 80-mesh Fraction (wt %)	Loss on Ignition (wt %)	Metal Concentrations (mg/kg) As	Se	Hg wet basis	Hg dry basis
In-Site Variability		Sample Number							
Aug 02/89	Camrose Creek	1	49.6	NA	7.21	4.1	0.153	0.021	0.042
Aug 02/89	Camrose Creek	2	56.7	NA	6.85	3.2	0.187	0.020	0.046
Aug 02/89	Camrose Creek	3	41.7	NA	4.76	3.8	0.168	0.016	0.027
Aug 02/89	Camrose Creek	4	68.8	NA	7.94	4.6	0.186	0.015	0.048
Aug 02/89	Camrose Creek	5	72.9	NA	7.60	3.8	0.174	0.016	0.059
Aug 02/89	Camrose Creek	6	42.0	NA	6.00	4.0	0.145	0.021	0.036
Aug 02/89	Camrose Creek	7	50.9	NA	8.33	4.7	0.207	0.023	0.047
Aug 02/89	Camrose Creek	8	75.0	NA	8.77	4.0	0.210	0.012	0.048
Aug 02/89	Camrose Creek	9	63.6	NA	7.41	4.6	0.202	0.015	0.041
Aug 02/89	Camrose Creek	10	71.3	NA	6.93	3.0	0.156	0.013	0.045
Aug 03/89	Unwin	1	20.3	46.8	0.56	5.3	0.021	0.006	0.008
Aug 03/89	Unwin	2	18.8	39.6	0.36	2.0	0.017	0.007	0.009
Aug 03/89	Unwin	3	17.6	31.3	0.43	2.2	0.022	0.007	0.008
Aug 03/89	Unwin	4	18.5	30.6	0.75	3.3	0.031	0.008	0.010
Aug 03/89	Unwin	5	18.0	20.9	0.29	3.4	0.030	0.006	0.007
Aug 03/89	Unwin	6	25.5	36.1	0.25	5.1	0.051	0.009	0.012
Aug 03/89	Unwin	7	23.1	32.4	1.09	10.6	0.053	0.010	0.013
Aug 03/89	Unwin	8	21.0	13.1	1.51	5.4	0.056	0.007	0.009
Aug 03/89	Unwin	9	39.9	22.5	1.48	5.0	0.050	0.006	0.010
Aug 03/89	Unwin	10	22.2	7.4	1.67	6.4	0.061	0.007	0.009
Vertical Distribution		Depth Range (cm)							
Sep 28/89	Camrose Creek	0 - 2	73.9	39.2	7.56	3.8	0.117	0.011	0.042
Sep 28/89	Camrose Creek	2 - 4	52.8	46.3	5.92	4.0	0.149	0.019	0.040
Sep 28/89	Camrose Creek	4 - 6	56.7	46.2	6.64	3.9	0.190	0.020	0.046
Sep 28/89	Camrose Creek	6 - 10	47.9	43.5	5.73	3.7	0.163	0.025	0.048
Oct 03/89	Unwin	0 - 2	25.5	19.3	0.66	3.0	0.030	0.005	0.007
Oct 03/89	Unwin	2 - 4	22.7	19.7	0.93	4.1	0.041	0.007	0.009
Oct 03/89	Unwin	4 - 6	19.8	13.8	0.81	3.7	0.035	0.006	0.007
Oct 03/89	Unwin	6 - 10	19.3	4.5	1.45	6.7	0.062	0.007	0.009

Table 2.24 Routine Monitoring Sediments: Extractable Heavy Metals

Date Sampled	Sample Site	0.5N HCl Extractable Metal Concentrations (mg/kg)								Aqua Regia Extractable Metal Concentrations (mg/kg)							
		Cu	Zn	Cd	Pb	Co	Ni	Cr	V	Cu	Zn	Cd	Pb	Co	Ni	Cr	V
Bottom Sediments																	
May 16/89	Hwy 611	9.04	26.40	0.13	4.36	2.66	6.82	2.84	5.15	13.64	53.8	< 0.7	(2)	6.8	19.4	18.3	19.4
May 16/89	Hwy 53	10.38	31.28	0.18	5.91	3.08	6.01	2.13	5.93	23.13	69.6	(0.2)	7	6.9	17.8	16.4	21.9
May 16/89	Camrose Creek	13.03	27.87	0.21	7.13	3.46	8.72	4.01	6.14	20.36	68.6	< 0.7	9	7.8	21.3	24.3	23.7
May 17/89	Hwy 872	6.43	16.05	(0.05)	6.47	2.88	4.61	0.78	0.17	9.84	44.1	< 0.7	6	6.3	11.9	10.7	18.1
May 17/89	Unwin	1.97	7.83	(0.06)	2.43	1.76	4.39	3.35	1.43	2.71	21.5	< 0.7	(3)	3.7	8.6	11.1	12.5
May 17/89	Battleford	2.53	8.89	0.10	3.06	1.73	3.09	0.83	1.94	4.31	27.6	< 0.7	(3)	4.4	9.7	10.5	18.0
Jun 20/89	Hwy 611	6.32	25.47	0.10	3.41	2.49	5.92	2.45	4.80	9.51	51.5	(0.2)	(2)	6.6	18.1	16.9	18.8
Jun 21/89	Hwy 53	9.56	28.54	0.13	6.57	3.34	5.83	2.05	5.41	16.67	70.4	(0.4)	7	7.9	19.0	18.4	24.0
Jun 22/89	Camrose Creek	11.63	27.20	0.22	6.90	2.65	5.34	1.14	5.68	18.13	68.6	(0.3)	9	6.6	15.8	15.2	25.9
Jun 23/89	Hwy 872	3.21	12.23	0.10	5.09	2.96	4.20	0.55	2.68	5.89	37.9	< 0.7	7	6.2	11.5	8.4	15.4
Jun 28/89	Unwin	1.39	8.07	(0.02)	2.31	2.01	3.19	0.53	1.52	2.59	23.2	< 0.7	(2)	4.2	8.0	7.5	12.3
Jun 28/89	Battleford	7.90	16.71	0.10	5.23	3.35	6.44	1.13	4.50	13.73	52.1	< 0.7	9	7.6	17.8	14.3	22.4
Jun 20/89	Battle Lake	4.72	22.81	0.11	2.26	1.97	5.85	3.19	5.41	7.79	48.3	< 0.7	< 4	7.3	19.4	21.4	25.1
Jun 21/89	Dried Meat Lake	16.01	38.97	0.27	9.34	3.22	7.88	1.74	8.43	23.27	76.2	(0.4)	7	7.6	17.1	16.6	28.4
Jun 23/89	Forestburg Res.	35.55	38.26	0.21	8.14	3.80	10.21	1.91	8.99	44.89	68.3	(0.3)	6	8.2	20.0	15.7	21.2
Aug 01/89	Hwy 611	6.49	28.95	0.12	3.53	3.28	8.64	3.49	6.46	9.25	47.3	< 0.7	(4)	6.6	17.1	19.9	23.5
Aug 01/89	Hwy 53	9.39	34.68	0.13	7.25	4.29	8.36	3.08	7.45	14.31	64.4	< 0.7	(3)	7.5	18.2	21.0	26.9
Aug 02/89	Camrose Creek	14.33	35.34	0.21	8.90	3.54	7.77	1.73	8.04	19.56	67.1	< 0.7	6	6.8	15.5	16.5	29.0
Aug 02/89	Hwy 872	3.46	15.26	(0.05)	4.77	3.25	5.18	0.83	3.33	5.40	33.9	< 0.7	4	5.4	9.3	10.0	19.7
Aug 03/89	Unwin	1.16	8.34	< 0.07	2.44	2.05	3.30	0.57	1.61	2.09	19.5	< 0.7	(3)	3.6	6.8	6.6	12.5
Aug 03/89	Battleford	4.84	15.44	< 0.07	5.71	3.66	6.87	2.37	4.94	8.39	40.5	< 0.7	5	7.1	18.7	27.2	27.0
Sep 26/89	Hwy 611	6.08	27.49	0.13	3.74	3.09	7.55	3.17	5.92	9.69	53.8	< 0.7	< 4	7.4	18.5	22.9	25.5
Sep 27/89	Hwy 53	9.67	34.62	0.15	8.05	4.38	8.20	2.86	7.54	16.21	75.8	< 0.7	(3)	9.1	20.6	23.4	33.2
Sep 28/89	Camrose Creek	14.44	34.82	0.22	9.33	3.42	8.66	2.98	8.72	21.08	75.9	(0.2)	7	7.8	19.1	21.4	31.7
Sep 29/89	Hwy 872	5.27	18.60	(0.06)	5.62	4.42	8.18	2.44	4.02	8.72	46.8	< 0.7	6	7.8	18.2	23.8	22.7
Oct 03/89	Unwin	1.49	9.74	< 0.07	3.11	2.27	3.68	0.70	1.92	2.54	22.8	< 0.7	(2)	4.0	7.7	7.7	13.9
Oct 03/89	Battleford	7.18	24.02	(0.06)	12.15	7.59	13.54	3.37	8.92	13.50	59.7	< 0.7	9	12.7	28.3	29.4	32.3
Feb 07/90	Hwy 611	8.72	37.69	0.23	3.48	3.53	9.77	3.73	7.60	13.60	65.7	(0.3)	< 4	8.1	21.0	21.6	27.0
Feb 06/90	Hwy 53	12.19	41.91	0.20	8.59	5.03	10.29	3.60	8.82	19.41	82.2	< 0.7	< 4	9.4	23.6	23.6	32.4
Feb 07/90	Camrose Creek	16.16	41.07	0.27	10.36	3.92	8.87	2.00	9.27	23.42	83.3	(0.4)	< 4	7.9	20.4	20.7	37.7
Feb 07/90	Hwy 872	6.59	25.28	(0.05)	11.64	6.43	20.81	14.14	5.60	10.53	57.0	< 0.7	10	10.4	33.7	45.9	22.7
Feb 08/90	Unwin	1.83	10.05	< 0.07	2.68	2.39	4.54	1.45	2.03	2.92	23.6	< 0.7	(2)	4.4	8.5	8.2	14.5
Feb 08/90	Battleford	6.13	18.18	(0.04)	3.53	3.14	6.38	1.31	4.38	8.50	39.9	< 0.7	< 4	6.1	12.8	12.8	25.6
Apr 23/90	Hwy 611	8.54	37.34	0.21	3.14	3.54	22.41	23.95	7.59	14.64	68.1	(0.2)	< 4	8.2	36.3	55.5	28.5
Apr 23/90	Camrose Creek	11.60	31.71	0.18	7.86	4.21	17.35	14.32	7.07	17.62	66.4	(0.5)	< 4	8.6	28.1	43.2	33.6
Apr 26/90	Unwin	1.32	8.39	(0.03)	2.16	1.88	6.26	5.40	1.63	2.36	21.5	< 0.7	< 4	3.8	9.9	14.0	16.1
Suspended Sediments																	
Apr 23/90	Hwy 611	18.56	58.14	0.43	9.65	4.01	11.40	4.37	9.89	32.28	115.5	(0.4)	< 4	9.2	30.7	36.2	45.3
Apr 24/90	Camrose Creek	20.18	45.47	0.38	11.34	4.87	15.71	11.07	8.67	31.71	102.5	(0.5)	< 4	10.5	35.2	48.9	44.0
Apr 25/90	Unwin	13.41	27.39	0.10	8.81	6.07	14.74	3.72	7.01	21.89	72.7	< 0.7	(1)	11.0	37.5	46.5	32.3

Table 2.25 Surficial Replicates and Core Sediments: Extractable Heavy Metals

Date Sampled	Sample Site		0.5N HCl Extractable Metal Concentrations (mg/kg)								Aqua Regia Extractable Metal Concentrations (mg/kg)							
			Cu	Zn	Cd	Pb	Co	Ni	Cr	V	Cu	Zn	Cd	Pb	Co	Ni	Cr	V
In-Site Variability		Sample Number																
Aug 02/89	Camrose Creek	1	13.24	36.80	0.23	8.61	3.64	7.84	1.97	8.11	18.80	69.1	< 0.7	(4)	7.4	17.4	15.5	27.9
Aug 02/89	Camrose Creek	2	17.21	42.40	0.32	10.23	4.36	9.25	2.26	9.14	24.27	84.2	(0.4)	(4)	8.6	21.9	22.2	37.0
Aug 02/89	Camrose Creek	3	10.45	30.36	0.12	6.84	3.69	7.33	1.74	6.44	14.32	58.4	< 0.7	(3)	7.0	14.7	14.8	25.9
Aug 02/89	Camrose Creek	4	16.26	41.94	0.34	9.79	4.19	9.79	2.20	8.91	23.64	82.8	< 0.7	(3)	8.5	21.2	21.2	37.7
Aug 02/89	Camrose Creek	5	16.04	41.64	0.30	9.88	4.05	9.39	2.14	8.92	23.25	81.9	< 0.7	(3)	8.1	20.7	19.5	32.9
Aug 02/89	Camrose Creek	6	12.99	36.13	0.24	9.81	4.12	8.96	2.06	7.98	18.09	68.0	< 0.7	(4)	7.6	17.8	15.9	26.0
Aug 02/89	Camrose Creek	7	17.05	42.63	0.38	10.85	4.35	9.82	2.23	9.24	23.65	82.3	(0.3)	7	8.4	20.6	17.9	31.3
Aug 02/89	Camrose Creek	8	16.87	42.13	0.33	12.36	4.10	9.01	2.31	9.13	23.66	81.0	< 0.7	9	8.0	20.6	19.0	32.1
Aug 02/89	Camrose Creek	9	14.90	39.86	0.28	8.96	4.02	8.96	2.22	8.61	20.93	75.2	(0.3)	6	7.8	18.5	16.4	28.7
Aug 02/89	Camrose Creek	10	14.72	39.32	0.23	9.12	4.01	8.75	2.10	8.43	20.61	75.2	< 0.7	5	7.8	18.6	15.9	27.4
Aug 03/89	Unwin	1	1.06	7.70	< 0.07	1.96	1.89	8.92	11.33	1.44	1.75	17.1	< 0.7	(2)	3.5	13.5	21.0	10.4
Aug 03/89	Unwin	2	0.95	7.13	< 0.07	1.40	1.91	15.78	24.44	1.28	1.38	15.6	< 0.7	(3)	3.0	11.2	15.7	8.2
Aug 03/89	Unwin	3	0.89	7.21	< 0.07	1.48	1.75	8.11	9.11	1.22	1.42	15.7	< 0.7	(2)	3.0	11.3	16.2	8.5
Aug 03/89	Unwin	4	1.44	9.35	< 0.07	2.43	2.26	9.84	10.57	1.82	2.58	21.8	< 0.7	(2)	4.2	16.7	26.7	12.6
Aug 03/89	Unwin	5	1.38	8.85	< 0.07	2.17	2.10	7.83	5.85	1.69	2.81	23.2	< 0.7	(3)	4.2	16.3	23.1	12.1
Aug 03/89	Unwin	6	2.60	12.88	< 0.07	3.44	3.07	6.59	2.99	2.77	4.81	33.4	< 0.7	(2)	5.9	13.9	13.4	16.7
Aug 03/89	Unwin	7	3.07	13.82	(0.05)	3.49	3.17	5.92	1.43	2.90	4.94	32.0	< 0.7	(2)	5.4	11.8	8.5	14.6
Aug 03/89	Unwin	8	2.35	13.13	0.08	3.01	3.31	5.46	1.24	2.86	4.42	31.9	< 0.7	(2)	5.8	11.6	8.0	14.2
Aug 03/89	Unwin	9	2.88	14.57	< 0.07	3.24	3.53	5.95	1.15	3.22	4.15	30.2	< 0.7	(3)	5.5	10.8	7.8	15.1
Aug 03/89	Unwin	10	2.90	15.16	< 0.07	3.35	3.85	6.22	1.40	3.51	4.17	30.5	< 0.7	(3)	5.8	11.1	8.0	16.0
Vertical Distribution		Depth Range (cm)																
Sep 28/89	Camrose Creek	0 - 2	15.90	11.20	0.26	10.03	4.72	52.54	78.50	9.59	22.04	76.8	< 0.7	(4)	9.3	84.3	163.0	36.8
Sep 28/89	Camrose Creek	2 - 4	14.35	39.95	0.21	9.78	3.72	14.77	9.23	8.59	19.55	71.3	(0.4)	(2)	7.9	25.9	34.8	31.4
Sep 28/89	Camrose Creek	4 - 6	16.75	44.78	0.26	11.04	3.96	12.91	6.43	9.71	22.45	78.7	< 0.7	6	8.1	23.5	27.4	30.0
Sep 28/89	Camrose Creek	6 - 10	13.87	39.34	0.20	9.83	3.82	8.54	1.95	8.08	19.59	71.4	< 0.7	(4)	8.2	18.0	17.4	30.7
Oct 03/89	Unwin	0 - 2	1.28	9.26	< 0.07	2.34	2.21	3.68	0.69	1.77	9.25	23.0	< 0.7	(2)	4.1	7.6	5.4	11.0
Oct 03/89	Unwin	2 - 4	2.28	11.36	(0.02)	3.08	2.97	18.98	23.31	2.66	3.36	24.0	< 0.7	(2)	4.7	29.9	52.5	12.6
Oct 03/89	Unwin	4 - 6	1.75	10.11	< 0.07	2.47	2.58	14.02	15.30	2.36	2.91	23.4	< 0.7	(1)	4.6	25.1	43.8	15.0
Oct 03/89	Unwin	6 - 10	3.47	16.73	(0.03)	4.42	3.95	7.37	2.27	4.28	5.97	38.2	< 0.7	(2)	7.0	15.0	17.9	25.7

2.5 CONCLUSIONS

The limiting step in biota and sediment analysis comes at sample preparation, where sample splitting, drying and sieving are labour intensive and tedious. This step may be an important factor in the large variance shown in biota analysis. For routine pollution monitoring, modern homogenizing facilities for biological samples would certainly be advisable. It is also advisable to improve the efficiency of sediment sample preparation by procuring additional sieving apparatuses that would allow several samples to be processed simultaneously; this step usually requires approximately one hour per sample with a single apparatus.

For biota analysis, the overall accuracy and precision for the determination of Cu, Cr, Ni, V, Zn, As and Hg in the certified reference materials used are very good. The averaged recoveries from spiked samples (including various subclasses of biota) are also generally acceptable (75 - 125%), but further calculations indicate that the RSD's of these recoveries are high, varying from 30 - 50% for six of the eight parameters tested. Moreover, RSD's derived from duplicates range from within 10% (for most parameters) to 25% (for a few parameters) at concentration levels significantly above the detection limits. The relatively poor precision for the analysis of field samples (spikes and duplicates) as compared to that for the certified reference materials might arise from the difficulties encountered in preparing homogeneous analytical samples from the wet biota samples received. Using a specialized, efficient apparatus for homogenizing biological materials might have circumvented some or all of these difficulties; such an apparatus was not available to WA&RB staff.

Poor precision in the determination of Se in biota indicates that this method is suspect and needs improvement. Methods for the determination of Cd and Pb in biota need to be established.

For sediment analysis, the analytical procedures for all parameters, except Se and Hg, performed well. The precision of sediment methods was generally less than ten percent for concentrations typically found in these samples. Poor recovery of Se from spiked samples and from CRM's indicates a need for improving that method; future investigations might focus on the extraction/digestion procedure and the pre-hydride generation steps. The accuracy of the Hg in sediment procedure cannot be evaluated conclusively from the limited amount of reliable QC data gathered on this parameter; further recovery studies for this method are therefore warranted.

Each of the two "heavy metals" extractions has its virtues and shortcomings. Compared to 0.5N HCl, Aqua Regia is more efficient and more widely employed; 0.5N HCl, however, yields more precise data and involves relatively simple procedures. For effective pollution monitoring, an investigator needs to detect appreciable changes in metal content above background levels. Either extractant studied here can provide such detection, so depending on the scope and intent of the monitoring program, the two could be of equal value.

In spite of this, the high detection limits and low recoveries observed for Cd and Pb using the present Aqua Regia method restricts the usefulness of this approach. Cadmium and Pb may be lost as volatile chloride compounds through the vigorous boiling employed in this extraction; such loss would make this method irreproducible as well as inaccurate, hence its high detection limits. A less vigorous approach, in which the sample is heated under reflux with the extractant, rather than heated to drive off water and HCl, might reduce or

eliminate the loss of these elements. Investigation into such reflux-based Aqua Regia extractions as alternatives to the present Aqua Regia extraction may be warranted.

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3. MULTI-MEDIA STUDY OF TRACE METALS IN THE BATTLE RIVER

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3.1 INTRODUCTION

Heavy metals occur naturally in sediment and rocks, but their environmental concentration may increase as a result of anthropogenic activities. Metals of anthropogenic origin are present almost exclusively as non-residual species (i.e. as opposed to residual metals which are entrained in the silica matrix of inorganic particles). Campbell et al. (1988) specify that these more reactive species of metals are also more likely to be bioavailable and that as a result bioaccumulation and biomagnification of some may occur. The term 'metals' is used subsequently to refer to the metals and metalloids considered in this study and which include arsenic, cadmium, copper, chromium, nickel, lead, selenium, vanadium, zinc and mercury.

There is no major heavy metal industry in the Battle River basin and severe contamination with metals is unlikely. However, there are many smaller potential inputs. Wind-blown dust and natural weathering are important natural sources of trace metals (Moore and Ramamoorthy 1984, Moore 1990) and are probably the main source of natural loads to the Battle River.

A considerable fraction of anthropogenic arsenic, chromium, copper, lead, mercury and nickel is derived from the burning of fossil fuels (Moore and Ramamoorthy 1984). Burning of coal, oil and gasoline probably represents the largest potential anthropogenic source of metals to the Battle River basin, particularly near major urban centres and in the vicinity of the coal-fired power plant. Coal mining activity may also contribute to the metal load of the Battle River. Municipal discharges integrate a wide spectrum of wastes from anthropogenic

activities and contribute to metal loads on surface waters (Moore and Ramamoorthy 1984). Considering their importance in the Battle River, wastewater discharges may contribute significantly to the anthropogenic loads in the river. Finally, many phosphate fertilizers and animal feed supplements contain a variety of trace metals or metalloids such as chromium, nickel, cobalt, selenium and copper.

3.2 METHODS

3.2.1 Study Design

Samples were collected at six sites along the Battle River (Figure 1.1, Table 3.1):

'Hwy 611', located near the headwaters is least affected by human activity, although there is substantial oil and gas exploitation in this area;
'Hwy 53', upstream of Wolf Creek, is influenced by agricultural activities in the upper portion of the basin;
'downstream (d/s) of Camrose Creek' is affected by the discharges from the four largest municipalities in the upper portion of the basin (i.e. Lacombe, Ponoka, Wetaskiwin, Camrose);
'Hwy 872' is located downstream of an area with active surface coalmining and a coal-fired power generating plant;
'Unwin' mainly influenced by agricultural activities and oil and gas exploitation, also a federal long-term monitoring site; and
'Mouth' reflects mainly agricultural activities in the Saskatchewan portion of the basin, upstream of the towns of North and South Battleford.

Longitudinal river surveys were conducted on 6 occasions (Table 3.2) to detect longitudinal or seasonal changes in contaminant levels which might result from natural or anthropogenic influences (e.g., municipal wastewater discharge, pesticide application).

Water and sediments were sampled each survey at all sites in the Battle River, except on April 23-25 1990, during spring run-off, when

Table 3.1 Multi-Media Sampling Sites in the Battle River (1989-1990)

Site Name	NAQUADAT Code	Distance (in km) from Source	Mouth
Hwy 611	00AL05FA0250	49	986
Hwy 53	00AL05FA0280	89	946
Downstream Camrose Cr.	00AL05FA0750	273	762
Forestburg Res. Nr. Inlet	00AL05FC0500	400	637
Hwy 872	00AL05FC1000	518	517
Unwin	00SA05FE1000[1] 0001[2]	826	209
Nr. Mouth	00SA05FF1000[1] 0001[2]	1030	5

[1] Alberta Environment codes
[2] Environment Canada codes

Table 3.2 Sampling Schedule for Various Media in the Battle River

Medium	May 16-17(1)	Jun 19-23(2)	Aug 1-3(3)	Sept 26-30(4)	Nov. 1(5)	Jan 15-19(6)	Apr 23-25(7)
Water	X	X	X	X		X	X
Bottom Sediment	X	X	X	X		X	X
Suspended Sediment							X
Aquatic Invertebrates		X		X			
Macrophytes/Algae			X				
Fish Tissue					X		X

(1) - before spring application of pesticides
- after spring run-off
(2) - after spring application of pesticides
- after release of most municipal discharges
(3) - open water background levels, low summer flows
(4) - after fall application of pesticides
(5) - collections from Forestburg reservoir, only
(6) - background levels under ice-cover
(7) - spring run-off

samples were collected only at Hwy 611, d/s Camrose Creek, and Unwin. Sediment samples from Battle Lake, Driedmeat Lake and the Forestburg Reservoir were collected once in June 1989.

Aquatic invertebrates were sampled in June and September 1989. Macrophytes and filamentous algae were also sampled at all sites, but only in August 1989. Fish were collected in November 1989 and April 1990 from the Forestburg Reservoir.

3.2.2 Sampling Methods

3.2.2.1 Water

Surface grab samples were taken from mid-channel. Upon return to the Millwoods Facility a sample aliquot was filtered on glass fibre (GMF) filters (particle retention 1.2 μm) followed by filtering on GFC (Sartorius) filters (particle retention 0.45 μm). The filtered sample was destined for dissolved metal analysis, the unfiltered sample for total metal analysis. Samples for mercury analysis were preserved with HNO_3 and K_2CrO_7, samples for the analysis of other metals with HNO_3; samples were shipped to the Water Analysis and Research Branch (WA&RB), Chemistry Division, Alberta Environmental Centre within 24 hours of collection.

3.2.2.2 Sediment

All equipment used in the collection of sediment samples for metal analysis consisted of plastic or teflon which had been soaked overnight in an acid bath (5% HCl). A brass Ekman dredge was the only metal instrument used in sample collection. Special care was taken not

to sample sediment which had been in direct contact with the metal walls of the dredge.

3.2.2.2.1 Longitudinal Surveys

Sediment samples from the Battle River and the lakes were collected with an Ekman Dredge (22.5 cm by 22.5 cm). Water was allowed to flow slowly out of the dredge, leaving surficial sediments undisturbed. Each sediment sample consisted of a composite of the top 1 cm sediment from at least 10 Ekman dredges. Sediment from all individual dredges was mixed in an acid-washed plastic bucket. Sufficient material was collected for split samples and for the analysis of particle size distribution and total organic carbon (TOC). Samples were frozen on dry ice immediately after their collection and stored in a freezer at -15°C until their shipment to WA&RB.

3.2.2.2.2 Horizontal Distribution

In order to determine the local variability of metal concentration, ten Ekman Dredge samples were collected downstream of Camrose Creek and at Unwin on August 1 and 3, 1989, respectively. The sediment from each dredge was treated as an individual sample.

3.2.2.2.3 Vertical Distribution

Five core samples were collected with plexi-glass corers downstream of Camrose Creek and at Unwin on September 26-30, respectively. These cores were sectioned up to a depth of 10 cm (i.e. 0-2 cm, 2-4 cm, 4-6 cm, 6-10 cm) and sections from corresponding depths

were combined to form one sample.

3.2.2.3 Suspended Sediments

Suspended sediment samples were collected from three sites during the last week of April, 1990 with a Sedisamp System centrifuge. The unit consists of an Alfa-Laval industrial clarifier with stainless steel centrifuge bowls (Envirodata Ltd., 1981). A submersible magnetic-drive pump was submersed approximately one meter near centre stream. The pump was attached to the centrifuge via 1.25 cm teflon tubing sheathed in 2 cm tygon. The centrifuge and pump were powered by a 3500 watt generator. A stainless steel splitter was mounted on the bowl housing to reduce sample flow to approximately 5 litres/min. All parts, including pump, bowl, lines and fittings were solvent washed (acetone, hexane, and dichloromethane) before the survey, and rinsed with large amounts of sample water prior to sample collection.

Samples of raw and centrifuged water were collected at each site to determine the efficiency of sediment recovery. An attempt was made to collect at least 100 g of suspended material at each site, and the run times were varied to give adequate sample size, dependent upon the river sediment concentration. Sampling times were 8 hours, 7 hours, and 3.5 hours at Hwy 611, d/s Camrose Creek, and Unwin, respectively. The same centrifuge bowl was used at all three sampling sites.

Samples were transferred from the centrifuge bowls to glass containers with teflon-lined lids immediately after centrifuge shutdown, and refrigerated until shipment to the laboratory. Sub-samples were subsequently removed for metals and pesticide analyses, and frozen in

appropriate containers.

3.2.2.4 Biota

In order to avoid contamination of samples with trace metals, all equipment used in the collection of biota samples for metal analysis consisted of plastic, teflon, or glass soaked overnight in an acid bath (5% HCl).

3.2.2.4.1 Invertebrates

Several methods were used to collect invertebrate samples for residue analysis. These included dredging, sieving, use of dipnets, and visual or tactile searching.

Invertebrates were sorted from organic and inorganic debris on Nitex netting (mesh size 2 mm and 5 mm) mounted on wood frames (50 cm x 50 cm). Specimens were sorted with teflon-coated forceps and stored in acid-washed 50 ml plastic vials with snap lids.

Taxon selection was based upon the abundance and size of the specimens. Amphipoda, and Sphaeriidae were collected from most sites in June and September (Table 3.3). Hirudinea, Tubificidae, Gastropoda, Unionidae, Chironomidae, and Simuliidae were collected in June or September, but only at a few sites. Unionidae samples consisted of soft tissue only, whereas all other invertebrate samples, including sphaeriid clams and snails, consisted of entire organisms. An estimated 30 to 50 g wet-weight of invertebrates from each taxon was rinsed in filtered river water and stored in coolers on dry ice. Samples were stored in a freezer at -15°C until their shipment to WA&RB. Duplicate samples of Amphipoda,

Table 3.3 List of Biota Samples Collected for Metal Analysis

	Hwy 611	Hwy 53	d/s Camrose	Forestburg Reservoir	Hwy 872	Unwin	Mouth
Amphipoda	M/S[1]	M-S	M-S	-	M-S	M-S	M-S
Sphaeriidae	M-S	M-S	-	-	M-S	M-S	M-S
Gastropoda	S	S	S	-	S	-	-
Unionidae	-	M	-	-	M-S	S	M-S
Hirudinea	M-S	M	M-S	-	M	-	-
Simuliidae	M	-	-	-	-	-	-
Tubificidae	-	-	M-S	-	-	-	-
Chironomidae	-	-	M-S	-	-	-	-
Potamogeton richardsonii	A[2]	A	A	-	A	A	A
Filamentous green algae	A	A	A	-	A	A	-
Fish	-	-	-	N[3]	-	-	-

[1] M - May 1989
S - September 1989
[2] A - August 1989
[3] N - November 1989

Gastropoda and Unionidae were collected at several sites in September.

3.2.2.4.2 Aquatic Plants

Potamogeton richardsonii was encountered at all sites. It was particularly abundant at the three upper sites, but became scarce at the three lower sites which made the collection of sufficient material difficult. Leaves and stems were separated from roots and treated as individual samples. Plant material was vigorously rinsed in river water before freezing on dry ice.

Mats of filamentous green algae and associated algae were also collected for analysis. Macroscopic debris was removed and algal material was vigorously rinsed in river water before freezing. No filamentous green algae were found near the Mouth on the day of sample collection (Table 4).

3.2.2.4.3 Fish

Fish collections were restricted to the Forestburg Reservoir (Table 3.3). Six Northern pike (Esox lucius Linnaeus) and five white suckers (Catastomus commersoni (Lacepede)) were collected with gill nets, sexed and measured. Axial muscles, without skin were removed from one side of each fish with acid washed, disposable plastic knives. Axial muscles or fillets from individual fish were frozen as separate samples. Pike sample #6 and #7 belong to left and right sides of the same fish; pike sample #7 was removed with a metal knife.

3.2.3 Laboratory Methods

A brief description of analytical methods is provided below. A detailed description of methods, methods development and quality control and quality assurance procedures may be found in Section 2 of this report, in Environment Canada (1988), and in Alberta Environmental Centre (1987).

3.2.3.1 Water

Methods used in analyses for As, Cd, Cr, Co, Cu, Pb, Hg, Ni, Se, V and Zn are listed in Table 3.4. Dissolved metal analysis was performed on filtered samples; total metal analysis on unfiltered samples.

3.2.3.2 Sediment and Suspended Solids

Analyses were done for non-residual Cd, Cu, Cr, Pb, Ni, V, and Zn while As, Se and Hg were analysed for their extractable forms. Analyses for all metals except Hg were performed on the freeze-dried sample portion that passed through an 80-mesh sieve (i.e. particles <180 μm). Two extraction techniques were applied to the samples analysed for non-residual metals: cold extraction in 0.5N HCl and a harsher hot extraction in Aqua Regia (three parts concentrated HCl and one part concentrated HNO_3). Samples for the determination of As, Se, and Hg were digested in HNO_3 and H_2SO_4. Non-residual metals were measured by inductively coupled plasma (ICAP); As and Se by hydride generation quartz furnace atomic absorption; and Hg by cold vapour atomic absorption.

Loss on ignition (LOI) of sediment samples was measured on

Table 3.4 Analytical Methods for Metals in Water

Metal	Preservation	NAQUADAT Code	Analytical Method or Instrument
As total	HNO_3	33005 L	Hydride Generation Quartz Furnace Atomic Absorption
Cd total	HNO_3	48009 L	Inductive Coupled Argon Plasma (ICAP) Emission Spectrometry
Cr total	HNO_3	24009 L	ICAP
Co total	HNO_3	27009 L	ICAP
Cu total	HNO_3	29009 L	ICAP
Pb extr.	HNO_3	82302 L	Atomic Absorption with Solvent Extraction
Hg total	HNO_3-$K_2Cr_2O_7$	80015 L	Cold Vapour Atomic Absorption
Ni total	HNO_3	28009 L	ICAP
Se total	HNO_3	34005 L	Hydride Generation Quartz Furnace Atomic Absorption
V total	HNO_3	23009 L	ICAP
Zn total	HNO_3	30009 L	ICAP
As dissolved	HNO_3	33102 L	Hydride Generation Quartz Furnace Atomic Absorption
Cd dissolved	HNO_3	48109 L	ICAP
Cr dissolved	HNO_3	24109 L	ICAP
Co dissolved	HNO_3	27109 L	ICAP
Cu dissolved	HNO_3	29109 L	ICAP
Pb dissolved	HNO_3	82103 L	Atomic Absorption with Solvent Extraction
Ni dissolved	HNO_3	28109 L	ICAP
Se dissolved	HNO_3	34102 L	Hydride Generation Quartz Furnace Atomic Absorption
V dissolved	HNO_3	23109 L	ICAP
Zn dissolved	HNO_3	30109 L	ICAP

freeze-dried, sieved (particles <180 μm) sediment dried overnight at 105°C and then ignited for 2 hrs. at 550°C. Sediment particle size analysis and measurements of organic matter and total organic carbon (TOC) were performed by Norwest Labs (Edmonton) on sediments collected for longitudinal surveys. The Leco-Furnace and the hydrometer method (McKeague 1978) were used to quantify TOC and for particle size analysis, respectively.

3.2.3.3 Biota

As a result of analytical difficulties, Pb and Cd were not analysed on biological tissue samples. All other metals were analysed for their total form and methods for fish tissue analysis were applied to all biological tissue samples.

Individual wet tissue samples of Amphipoda, Sphaeriidae, Gastropoda, Chironomidae and Simuliidae were crushed and mixed; samples of Hirudinea, Unionidae and fish were chopped with a teflon spatula and mixed; samples of Tubificidae were treated whole. Macrophytes were freeze-dried and crushed.

Cadmium, Cr, Cu, Ni, Pb, V, and Zn analyses were performed on wet invertebrate or fish tissue, or freeze-dried plant material. Samples were digested in HNO_3 and H_2SO_4. Metals were analysed by the ICP method.

Tissue for As, Se, and Hg analysis was digested with H_2SO_4 and HNO_3. Digests were measured with the same procedures used for sediment extracts. Analyses were performed on wet invertebrate or fish tissue and on freeze-dried plant tissue. Wet plant tissue was used for the analysis of Hg.

The moisture content of all sediment and biota samples was determined so that metal levels could be expressed in a uniform measure (weight per dry weight) for all media.

3.2.4 Special Considerations Regarding Field and Laboratory Methods

3.2.4.1 Sampling Methods

The collection of water, settled or suspended sediments did not present any unexpected problems. However, the collection of single taxon aquatic invertebrate samples for tissue analysis was very time-consuming and labour intensive Table 3.5. Reasons for this situation and details on methods which improved collection efficiency are outlined below.

AQUATIC INVERTEBRATES

Monitoring of contaminants in invertebrates in marine and estuarine environments has been popular for many years (e.g., Farrington et al. 1983, Bryan et al. 1985). The most frequently sampled marine invertebrates are large, abundant (often colonial) and often of economic value (e.g., mussels, oysters). Compared to marine environments, considerably less monitoring of contaminants in invertebrates has been carried out in fresh water environments. The lack of fresh water species with a wide geographic distribution and analogous size and distribution patterns as marine species has impeded the rapid development of a body burden data base for fresh waters. Campbell et al. (1988) also invoke the diversity of freshwater environments as a reason for the poor knowledge of bioaccumulation ranges for species in North American freshwaters.

Table 3.5 Sampling Methods and Average Time Required to Sample Various Media in the Battle River

Medium	Sampling Method	Unit Sampling Time *
Water	- Grab	< 5 min.
Sediment	- Ekman Dredge	1/2 hour
Suspended Sediments	- Sedisamp	3 hours
Invertebrates	- Ekman Dredge - Dipnets, Screens, etc. - Hand Pick	> 4 hrs.
Macrophytes and Filamentous Algae	- Hand Pick	5 min.
Fish	- Gill Nets	15 min.

* person hour per sample

Most invertebrates in Alberta rivers are small and the efficient collection of a sufficiently large mass of tissue for chemical analysis became a focal point of the field work in the Battle River. Although initial taxon selection was based upon abundance and size of specimens, not all taxa proved to be equally easy to collect (e.g. Table 3.6), and each taxon required different sampling techniques.

Amphipoda (Gammarus lacustris and Hyalella azteca) were by far the most desirable invertebrates in the Battle River for mass-collections. At all sites it was easy to collect large numbers of specimens by sweeping a dipnet just above the bottom sediments or among weed beds. Only large specimens (i.e. $\geq$0.5 cm) were sorted from the Nitex screens. On average, sample collection required one and a half person hours per sample.

Sphaeriidae (Pisidium and Sphaerium) were encountered at all sites, except downstream of Camrose Creek. However, their distribution was rather patchy and considerable time was spent gathering and sieving sediments. Sieved samples were placed on Nitex screens which were immersed carefully in the river. The gentle water current removed most organic debris and left the heavier sphaeriids on the screen. In fall, water levels had dropped considerably at downstream sampling sites and sphaeriids could be spotted by their trails in the sand. Although the family Sphaeriidae was encountered at most sites in the Battle River, there was a shift from site to site in the proportion of Sphaerium and Pisidium (the latter being more abundant at upstream sites). Sample collection time for sphaeriids ranged from 2 to 4 person hours per sample.

Table 3.6 Suitability of Invertebrates from the Battle River for Multi-Media Monitoring - Rating Based on Field Criteria Only *

Criteria	Amphipoda	Sphaeriidae	Unionidae	Hirudinea	Gastropoda	Simuliidae	Chironomidae	Tubificidae
Abundance	++	0	0	0	0	0	0	0
Size of Organism	+	-	++	0	+	--	--	--
Distribution	+	0	0	0	0	0	0	0
Sorting Method	+	++ to +	++	+	0	--	--	--

++ Very Good
+ Good
0 Variable
- Poor
-- Very Poor
* See discussions in text for details

Unionidae (Anodonta grandis, Lampsilis radiata, Lasmigona complanata) were particularly attractive because of their large individual size (Table 3.6). However, as a result of their patchy distribution and low population density, much time was spent searching for specimens, particularly at upper sites. At lower sites and especially in the fall, it was possible to spot the clams by their trails on the sand in shallow waters. This definitely reduced the collection time which ranged from 5 minutes to 2 hours per clam.

Gastropoda (mostly Physa, some Lymnaea) were encountered in sufficiently large numbers for sample collection at several sites in the fall. Snails were separated from the vegetation by shaking the plants in a bucket of water and then pouring the contents of the bucket onto a Nitex screen.

Sampling of Hirudinea (Erpobdellidae, Glossiphonidae) was complicated by low numbers, uneven distribution and relatively small sizes for most specimens. Collection relied primarily on visual search among aquatic vegetation, rocks and decaying logs and was often exceedingly time consuming and laborious. The high mobility of Erpobdellidae made their sampling even more difficult. Collection time ranged from 4 to 6 hours per sample.

Simuliidae were sampled rather opportunistically at Hwy 611 where very dense populations coated submersed aquatic plants. Blackfly larvae and aufwuchs were gently scraped off the vegetation into plastic containers. After approximately half an hour most larvae were clinging to the container walls. Water and debris were poured off and replaced with clean water. Remaining debris was removed manually. Larvae were

wiped into a sieve and rinsed. Approximate sample collection time was 5 hours. Blackfly populations at other sites were not as abundant and many larvae had reached the pupal stage (not mobile, not able to fasten themselves). It was impractical to obtain clean samples of the tiny larvae in a reasonable amount of time.

Despite their small size, a special effort was made to collect Chironomidae (Chironomini) and Tubificidae downstream of Camrose Creek where those organisms appeared to be most abundant. These midges and worms are particularly attractive as potential tools for the monitoring of biologically available sediment contaminants because they utilize sediment as a food source and live in intimate contact with it. Chironomini were collected by stirring mud and water in buckets, letting the material settle for a few seconds, then pouring the supernatant and surficial mud on Nitex screens. Although this method is effective , the collection of a suitable sample weight was inhibited by the low larval densities. Tubificids were obtained in a similar manner as chironomids. This procedure was extremely time consuming, but yielded relatively clean specimens. Attempts were made to extract worms passively by placing sediment over a screen which barely touched the water in an underlying pan. The expectation was that worms would migrate out of the sediments into the water. This method was slow and inefficient. Worms which migrated to the pan were coated with fine silt and mucus which made them hard to spot and difficult to clean. Tubificid and chironomini ingest mud as part of their food and defecate almost continuously, consequently it was very difficult to produce clean samples, free of sediment particles. Collection of tubificid and chironomid samples required at

least 10 hours each and yielded insufficient material for complete residue analysis.

The average collection time for tissue samples from all invertebrate groups exceeded 4 person hours per sample (Table 3.5). An average of 5 individual invertebrate taxa was collected per site. The crew involved in the collection of benthic invertebrate samples ranged from 4 to 7 people.

AQUATIC PLANTS

Compared to invertebrates, collection of aquatic plants was a rapid and easy process. The main effort was spent in searching for specimens of the appropriate species; these were usually abundant in the Battle River although less so at the three downstream sites.

Removal of aufwuchs and sediment by vigorously shaking the plant parts in water was somewhat subjective as the aufwuchs community was sparse and thus not readily visible; the knotty rhizome structure of the roots may have retained small amounts of sediments, not visible to the unaided eye. However, the macrophyte samples were considerably easier to clean than most invertebrate samples or filamentous algae samples.

The average time involved in collecting aquatic plants was less than 5 minutes per sample (Table 3.5).

FISH

High population densities of white sucker and pike in the Forestburg Reservoir ensured the rapid collection of an adequate number of fish. Adequate muscle and liver sample material was easily obtained (Table 3.5). Teeth of disposable knives wore off quickly against the

hard fish scales and several knives were needed to obtain each tissue sample for metal residue analysis.

3.2.4.2 Laboratory Methods

Since analytical methods development was required for metals, some comments regarding the implications of methods choice on metal concentrations measured in various media are included here. A detailed discussion on methods development for analysis of sediment and biological samples is included in Section 2.

WATER

Upon examination of the data set for dissolved and total metals, an aberration became apparent in the data for Zn and Ni. For these two metals, dissolved concentrations always (Zn) or frequently (Ni) exceeded the total concentrations. The cause of the problem was traced to contamination during the filtering of the samples. GMF (WHATMAN Multigrade-150) and GFC (WHATMAN borosilicate glass Fibre) filters released trace amounts of these metals to the samples. The degree of contamination was compounded because the high suspended solids concentration in the Battle River required that several filters be used. Because of this contamination problem, further comments regarding dissolved zinc are not included.

SEDIMENTS

Several choices were made regarding the methods for preparing the samples and extracting non-residual metals (Section 2). Each of these choices has contributed to the enhancement of the quality of the

data. At the same time, each choice considerably narrowed the size of the literature data base against which Battle River data can be compared, since data can only be compared to other data generated with equivalent methods. Although several authors have published metal residue data derived from hot extraction in Aqua Regia or cold extraction in 0.5N HCl, few also chose to perform these extractions on sieved sediments (i.e. fraction <180 μm).

When comparing non-residual metal levels measured on total and sieved sediment samples, it is important to keep in mind that metal concentrations for sieved sediments per unit weight are greater than the concentration which would have been measured on the unsieved (total) sediment sample (e.g., Steele and Coughlin 1982).

To a certain extent, the choice of the extraction technique for non-residual metals is arbitrary as there is no single 'correct' extraction method (see Section 2). Hot extraction in Aqua Regia is more aggressive than the cold extraction in 0.5N HCl. The first method may leach a certain amount of metals from the mineral portion of the sample, whereas the latter may not release all non-residual metals. Either method may be used in a monitoring program, but it should be used consistently. The cold extraction may be preferable over the hot extraction for some metals. In this study the hot extraction yielded unreliable results for Cd and Pb (see Section 2.5) and only results from the cold extraction should be considered.

BIOLOGICAL SAMPLES

Certain aspects of biological sample processing require further

clarification. Benthic invertebrate samples were rinsed in the field with river water, but some samples collected in May (especially Chironomidae and Oligochaeta) still contained fine silt and sand. In an attempt to remove this material, samples were thawed and rinsed with distilled water in the laboratory. Although this procedure has been used in other body burden studies (e.g., Wageman et al. 1978) it could potentially remove metals from leached cell fluids. Exceptional care was taken with field cleaning of samples of burrowing taxa in September and these samples were not rinsed in the laboratory.

Digestion procedures for fish tissue were applied to all biological tissue samples. They involved rather vigorous mixed acid digestion of biological tissue and the extraction of residual metals contained in ingested sediments. The appropriateness of applying these methods to invertebrate organisms which utilize sediments as a food source is debatable. From the point of view of body burden determination it may be undesirable to include the residual metals contained in the mineral portion of the gut-content. However, from the point of view of transfer of metals to higher trophic levels in the foodchain it may be more meaningful to use the entire organism, including gut-content. Some authors advocate cleaning the gut-contents by placing organisms in acid-washed sand for several days, then in water for a day (Bryan et al. 1985). This method only eliminates some residual metals (e.g., Chapman 1985, Hare et al. 1989), and may reduce actual body burdens of metals with high clearing rates (for information on clearing rates see Moore and Ramamoorthy 1984).

Traditionally, fish muscle tissue residue levels are given for

wet tissue as this is more meaningful from the point of view of human consumption. In aquatic invertebrates and plants, expressing residue levels for dry tissue is preferable because there are large variations in moisture levels among different taxa or even within the same taxon. Residue levels for wet weights are of little comparative value among samples. In the Battle River, all Hg residue levels were determined on wet tissue samples and results are given for wet weights. For the remaining metals, wet tissue was used for fish and invertebrates and results were converted afterwards to dry weights, whereas dry tissue was used for plant measurements. To improve consistency and to reduce complications associated with wet weight to dry conversion (e.g., when residue levels are below the detection limit - see section 2), it would be preferable to perform all analyses on dry tissue. However, this is not always practical or desirable. For example, dried fish tissue often has a sticky, elastic texture because of its fat content. Such tissue is difficult to homogenize and sample (pers. comm. D. Lucyck).

3.3 RESULTS AND DISCUSSION

3.3.1 Water

Levels of total and dissolved As, Cu, Cr, Cd, Ni, Zn, Se, Pb and total Hg were monitored at the multi-media sites according to the schedule outlined in Table 3.2. In addition, metal levels were also monitored on a monthly basis at the six multi-media monitoring sites and at several other sites as part of another water quality study on the Battle River.

Levels of Hg, Se and Pb were generally below the detection limit

(Table 3.7). Only one sample collected at Hwy 872 on January 10, 1990 had detectable (0.0001 mg/L) levels of Hg. Total Pb concentrations were always below detection except on April 10, 1990 when lead was detected downstream of Camrose Creek, at Hwy 872 and at Unwin (0.004, 0.013, and 0.003 mg/L, respectively). Nine out of the 47 samples collected in the Battle River had measurable levels of dissolved Pb (maximum recorded concentration: 0.010 mg/L at Unwin on May 4, 1990). Selenium was below the detection limit at Hwy 611 and Hwy 53, but measurable amounts of total and dissolved Se were recorded at other sites. The highest concentration (0.0010 mg/L) was recorded at Unwin on June 28, 1989; no other concentration exceeded 0.0002 mg/L.

Longitudinal and seasonal patterns of metal concentration were examined for the remaining metals. As mentioned earlier (Section 3.2.4.2) contamination with Zn and Ni during the filtering resulted in unreliable data for the dissolved fraction of these metals, and only their total concentrations are discussed below.

3.3.1.1 Influence of Discharge on Metal Concentrations

It is well-known that metal concentrations in water are highly dependent upon river discharge and suspended sediment concentration. Of the total metal load transported by a stream at a given time, the fraction which is in the dissolved phase will depend on the concentration and nature of suspended sediments (e.g. Feltz 1980).

In the Battle River, concentrations of non-filterable residue (NFR) were significantly correlated to river discharge (Q), and total As, Cu, Cr, Ni and V showed significant positive correlations with river

Table 3.7 Median Metal Concentrations (mg/L) in Water at Multi-Media Monitoring Sites in the Battle River (May 1989 to April 1990)

	Hwy 611	Hwy 53	Below Camrose Cr.	Hwy 872	Unwin	At Mouth
Cu Diss.	0.001	0.002	0.002	0.003	0.003	0.003
Total	0.001	0.002	0.002	0.004	0.003	0.002
Zn Total	0.003	0.003	0.003	0.005	0.003	0.004
Cd Diss.	<.001	0.001	0.001	0.002	0.002	0.002
Total	<.001	0.001	0.002	0.002	0.002	0.002
Pb Diss.	<.002	<.002	<.002	<.002	<.002	<.002
Extractable	<.002	<.002	<.002	<.002	<.002	<.002
Co Diss.	<.001	0.001	0.001	0.001	0.002	0.002
Total	<.001	<.001	0.001	0.002	0.002	0.002
Ni Diss.	0.003	0.004	0.005	0.008	0.008	0.007
Total	0.002	0.004	0.006	0.008	0.007	0.007
Cr Diss.	0.001	0.002	0.002	0.002	0.002	0.003
Total	0.002	0.002	0.002	0.003	0.003	0.003
V Diss.	0.002	0.003	0.003	0.003	0.004	0.004
Total	0.003	0.004	0.005	0.005	0.006	0.006
As Diss.	0.0010	0.0013	0.0012	0.0012	0.0011	0.0011
Total	0.0016	0.0020	0.0030	0.0019	0.0027	0.0027
Se Diss.	<.0001	<.0001	<.0001	0.0001	0.0001	0.0001
Total	<.0001	<.0001	<.0001	<.0001	<.0001	<.0001
Hg Total	<.0001	<.0001	<.0001	<.0001	<.0001	<.0001
NFR	5	7	22	17	26.5	21.5

Sample size: - dissolved metals: n = 28
- total metals: n = 40

discharge and NFR (Table 3.8, Figure 3.1 to 3.5). However, total Cd was not correlated to river discharge or to NFR. Dissolved Cu was correlated to NFR, but correlations of other dissolved metals with river discharge or NFR were not significant (Table 3.8).

The relationships between river discharge, NFR and particulate metal levels in water are well illustrated in the case of As in the Battle River (Figures 3.1 and 3.2). The degree with which flow and NFR influence total As concentrations was different between the 3 upper (i.e. Hwy 611, Hwy 53 and d/s Camrose Creek) and the 3 lower sites (i.e. Hwy 872, Unwin, near mouth). Discharge explained 32 % of the sample variance in the entire data set [r^2 = 0.32, linear regression $\log_{10}Q$ versus $\log_{10}$(total As)]. However, discharge was a more important determinant of total As levels at the three lower sites (r^2 = 0.63) than at the three upper sites (r^2 less than 0.01). During periods of high flow, when NFR levels were highest, 80 to 85 % of the total As occurred in the particulate form at the lower sites, compared to 16 to 60 % at the upper sites (Figure 3.1 and 3.2). As flows and NFR levels decreased, the proportion of dissolved As increased and by mid-summer most As was in the dissolved form. The proportion of the dissolved and particulate fractions of other metals evolved in a similar way, but the variability in the data set was larger.

3.3.1.2 Longitudinal Trends

Longitudinal trends were apparent in the distribution of most metals. During high flows, at times when NFR levels are highest, there was a distinct increase in metal concentration in a downstream direction

Table 3.8 Correlation of Metal Levels with Discharge and NFR

	Variable	Correlation Coefficient[1] (r)	Degrees of Freedom (df)	Significance of $P<0.01$[2,3]
1) Correlation of metals and NFR with discharge				
	NFR	0.636	38	S
Total	As	0.564	38	S
	Cu	0.444	38	S
	Cr	0.528	38	S
	Cd	0.000	38	NS
	Ni	0.555	38	S
	V	0.487	38	S
	Zn	0.435	38	S
Dissolved	As	0.000	26	NS
	Cu	0.464	26	NS
	Cr	0.118	26	NS
	Cd	0.105	26	NS
	Ni	0.219	26	NS
	V	0.322	26	NS
2) Correlation of metal levels with NFR				
Total	As	0.745	56	S
	Cu	0.839	56	S
	Cr	0.667	56	S
	Cd	0.160	56	NS
	Ni	0.764	56	S
	V	0.840	56	S
	Zn	0.668	56	S
Dissolved	As	0.287	45	NS
	Cu	0.479	45	S
	Cr	0.062	45	NS
	Cd	0.120	45	NS
	Ni	0.106	45	NS
	V	0.148	45	NS

[1] calculated on log-transformed values

[2] $P<0.01$ df = 38, r tabulated = 0.403
df = 26, r tabulated = 0.479
df = 45, r tabulated = 0.372
df = 56, r tabulated = 0.336

[3] S, significant
NS, not significant

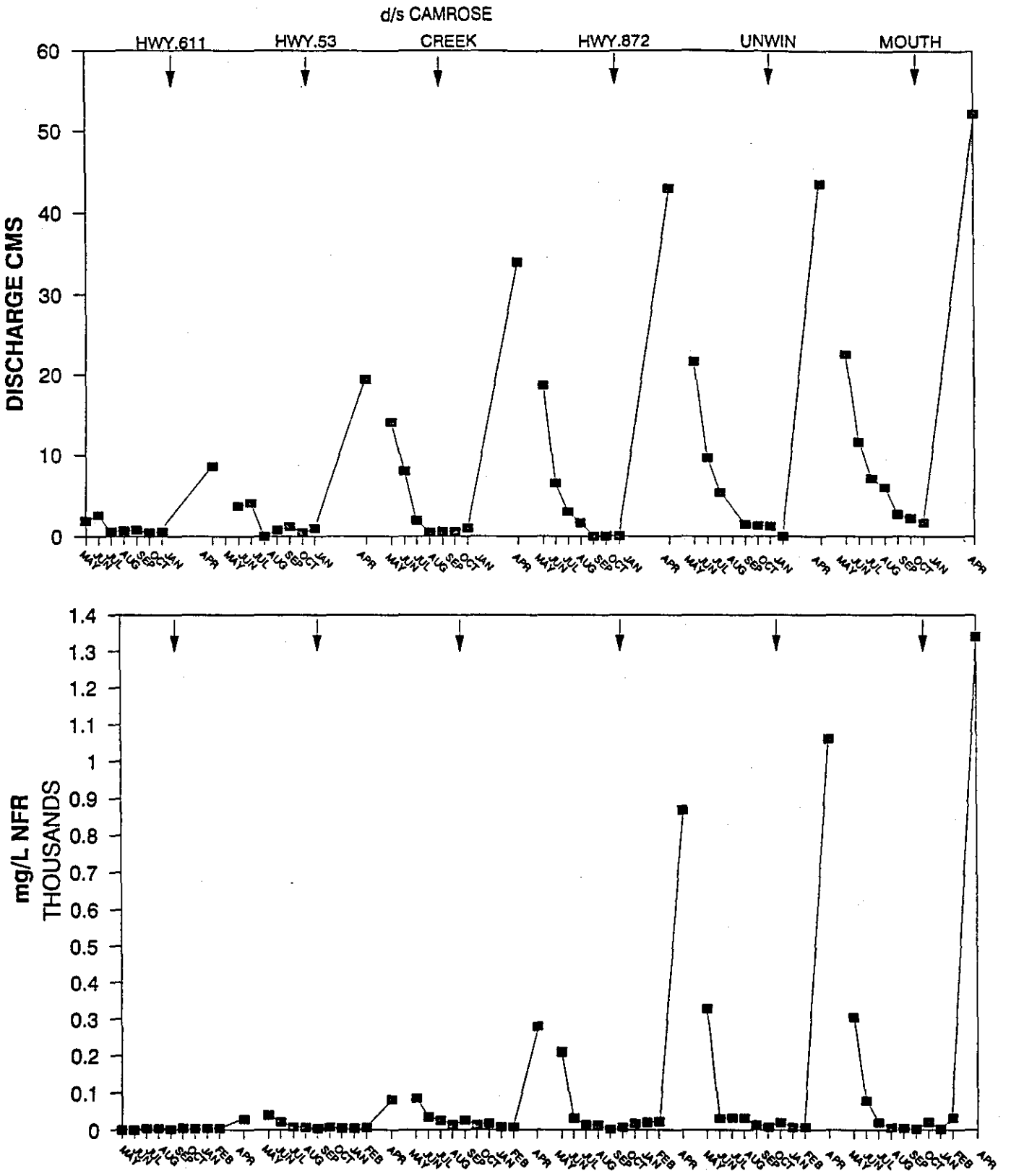

Figure 3.1 DISCHARGE AND NON-FILTERABLE RESIDUE LEVELS (NFR) IN THE BATTLE RIVER (MAY 1989-APR 1990)

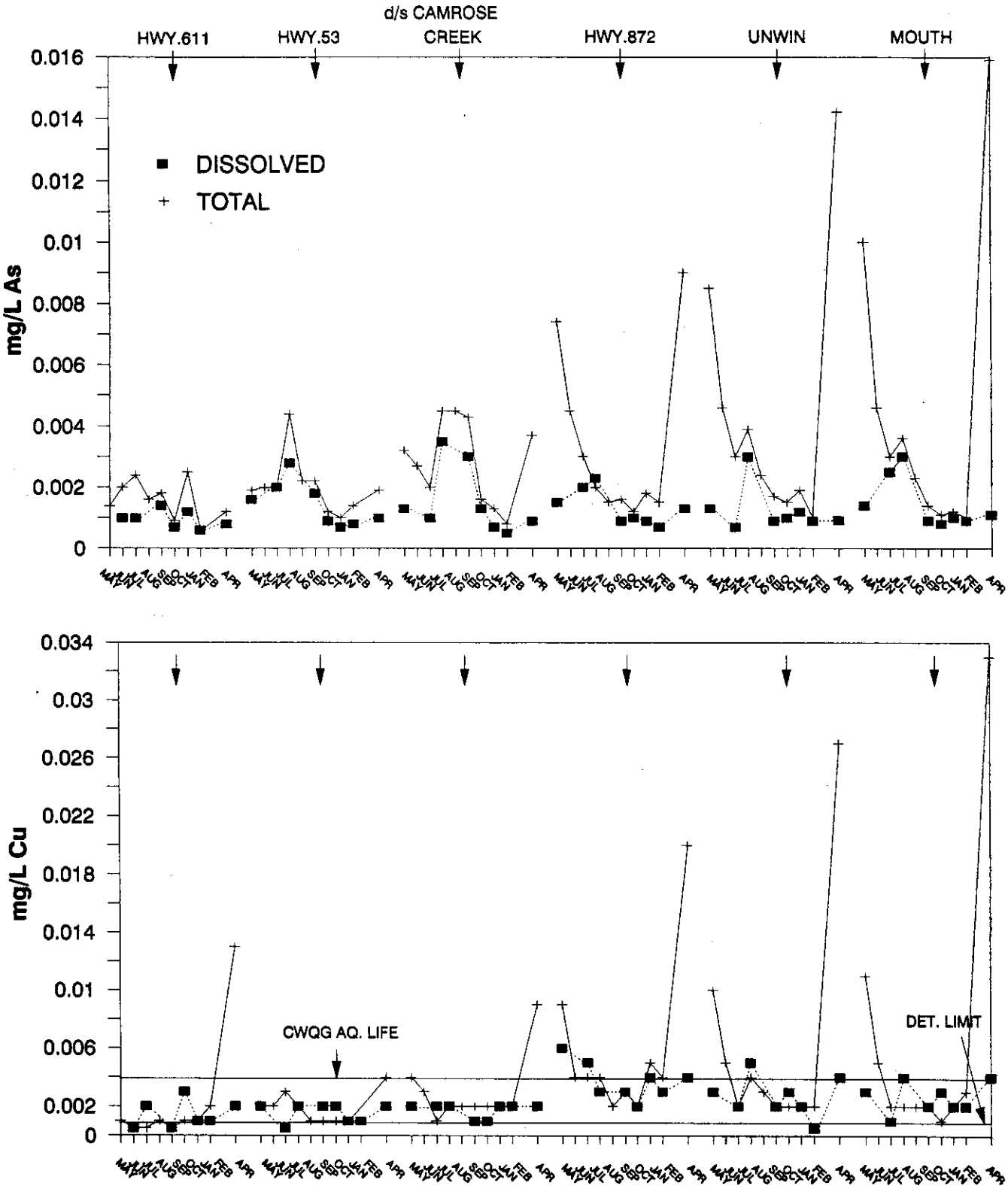

Figure 3.2 LEVELS OF TOTAL AND DISSOLVED ARSENIC AND COPPER IN BATTLE RIVER WATER (MAY 1989-APR 1990)

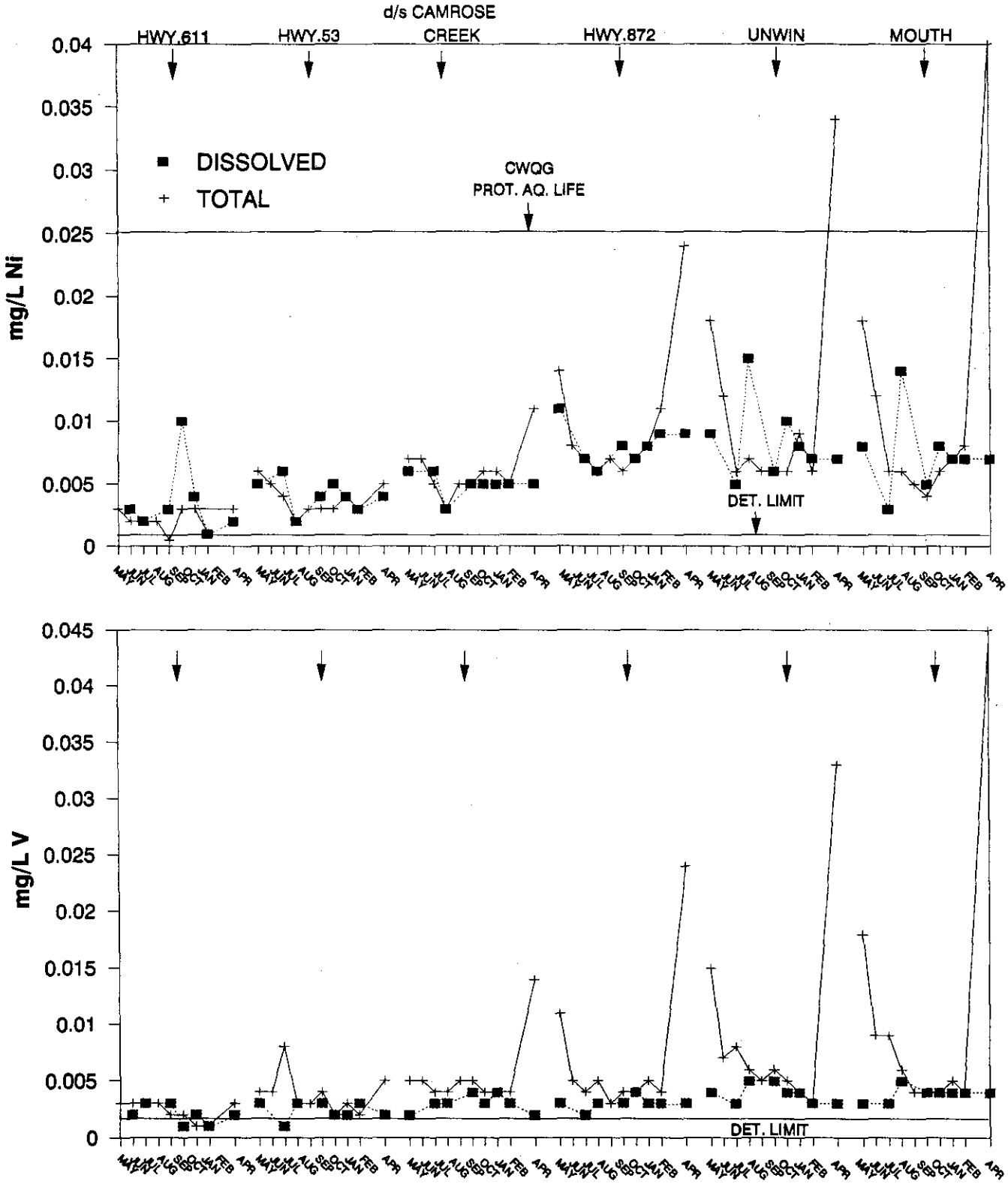

Figure 3.3 LEVELS OF TOTAL AND DISSOLVED NICKEL AND VANADIUM IN BATTLE RIVER WATER (MAY 1989-APR 1990)

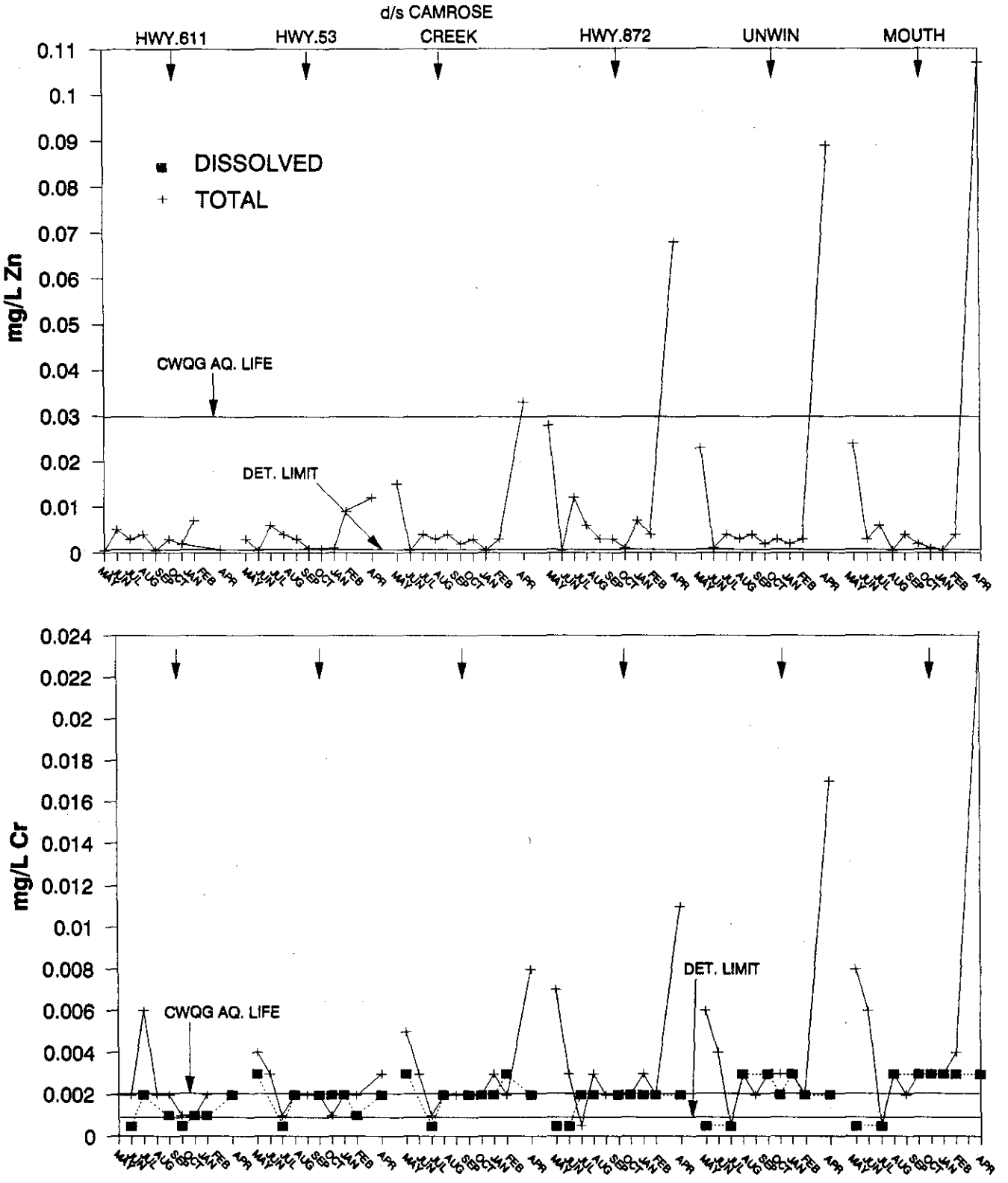

Figure 3.4 LEVELS OF TOTAL AND DISSOLVED ZINC AND CHROMIUM IN BATTLE RIVER WATER (MAY 1989-APR 1990)

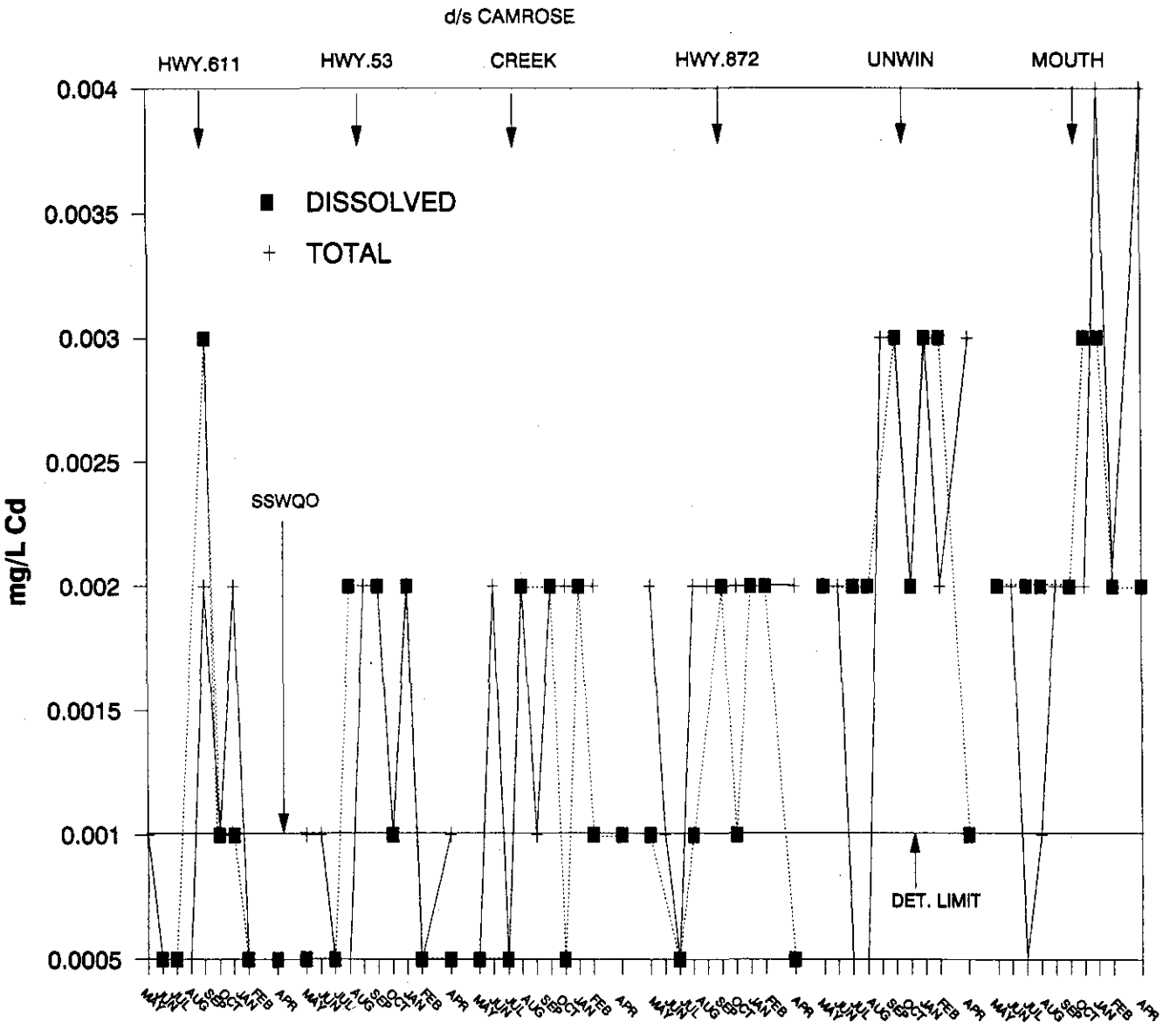

Figure 3.5 LEVELS OF TOTAL AND DISSOLVED CADMIUM IN BATTLE RIVER WATER
(MAY 1989-APR 1990)

(Figures 3.2 to 3.5)[1]. However, during low flows, at times when NFR levels were low, longitudinal differences among sites were less pronounced. Median concentrations over the entire sampling period (May 1989 to April 1990) increased gradually in a downstream direction, although the progression of the increase varied among metals (Table 3.7). For some metals such as Cu, Ni and Zn, highest median concentrations for the dissolved fraction were recorded at Hwy 872 (i.e. downstream of the Alberta Power Ltd. plant and associated coalmining activity). In contrast, the median concentration of total As was lower at Hwy 872 than at most other sites. An identical longitudinal pattern was exhibited by NFR values (Table 3.7). For other metals such as Cr, V, and Cd, longitudinal increases in dissolved or total median concentrations were more subtle, often showing only an increased frequency of detectable concentrations in downstream direction. One possible reason that longitudinal trends for Cr, V and Cd are subtle is that the level of these metals is at the detection limit or within the quantitative detection limits (defined as 10x detection limit), where precision of measurements is poor. The data suggest that instrumental methods with better detection limits such as ICP-MS are required for the monitoring of these trace elements (pers. comm. S. Wu).

[1] These Figures also show the method detection limit and the most restrictive of the Alberta or Saskatchewan surface water quality objective (ASWQO, SSWQO), the Canadian Surface Water Quality Guidelines (CWQG) or the Prairie Provinces Surface Water Quality Objectives (PPWBO). Refer to Table 3.19 for further details.

3.3.1.3 Seasonal Trends

Seasonal changes in total or dissolved metal concentrations other than those related to changes in discharge and suspended sediment concentrations were not readily apparent. Arsenic was an exception. At all sites, but especially downstream of Camrose Creek, dissolved As concentrations were highest during July, August and September (Figure 3.2).

3.3.2 Bottom Sediments

The importance of sediment organic matter content and grain size distribution on trace metal concentrations in sediments is well documented in the literature. According to Campbell et al. (1988), exchangeable and adsorbed metals seldom exceed a few percent of the total metal concentration, whereas metals bound to organic matter or associated with iron/manganese oxides dominate the partitioning of the non-residual component. Because there is a general increase in metal concentration from coarse to finer grained sediment fractions, Forstner and Wittman (1981) state that a correction for grain-size effects is necessary before a comparison of metal data in fluviatile deposits is possible.

Based on grain size and organic content, there were pronounced differences in the nature of the sediments sampled at the six Battle River sites (Table 3.9) and these differences alone could explain longitudinal patterns in metal levels. The silty sediments, rich in organic matter, which were sampled at the three upper sites are more likely to have a greater capacity to fix trace metals than the sandy substrates, poor in organic matter, sampled at the three lower sites.

Table 3.9 Summary Statistics for Metals (mg/kg), Particle Size Distribution and Organic Content (%LOI) of Battle River Sediment Samples

	ANALYSES ON SAMPLE FRACTION < 180 µm									TOTAL												
	0.5N HCl									Aqua Regia								H_2SO_4-HNO_3			Particle Size Distribution and % C			
	%LOI	Cu	Zn	Cd	Pb	Co	Ni	Cr	V	Cu	Zn	Cd	Pb	Co	Ni	Cr	V	As	Se	Hg	% Sand	% Silt	% Clay	% C
A. LONGITUDINAL AND SEASONAL SURVEYS																								
Hwy 611																								
Min	7.51	6.08	28.47	0.10	3.14	2.49	5.92	2.45	4.80	9.25	47.3	0	0	6.6	17.1	16.9	18.8	3.3	0.228	0.007	58.6	21.2	11.2	0.97
Max	12.11	9.04	37.69	0.23	4.36	3.54	22.41	23.95	7.60	14.64	68.1	0.3	4	8.2	36.3	55.5	28.5	4.4	0.584	0.015	66.6	28.2	14.2	3.41
Mean	9.30	7.51	30.56	0.15	3.61	3.10	10.19	6.61	6.25	11.72	56.7	0.1	2	7.3	21.7	25.7	23.7	3.6	0.402	0.011	63.2	24.2	12.7	2.44
Std. Dev.	1.82	1.23	5.03	0.05	0.38	0.40	5.60	7.77	1.09	2.27	7.5	0.1	1.6	0.7	6.6	13.4	3.6	0.4	0.165	0.003	3.54	2.7	1.12	1.04
No. Samples	6	6	6	6	6	6	6	6	6	6	6	6	6	6	6	6	6	4	4	6	4	4	4	4
Hwy 53																								
Min	6.69	9.39	28.54	0.13	5.91	3.08	5.83	2.05	5.41	14.31	64.4	0	0	6.9	17.8	16.4	21.9	7.6	0.129	0.010	66.6	6.2	7.2	0.34
Max	7.91	12.19	41.91	0.20	8.59	5.03	10.29	3.06	8.82	23.13	82.2	0.4	7	9.4	23.6	23.6	33.2	8.9	0.324	0.018	86.6	20.2	13.2	1.59
Mean	7.33	10.24	34.12	0.16	7.27	4.02	7.74	2..74	7.03	17.95	72.5	0.1	4	8.2	19.8	20.6	27.7	8.3	0.197	0.014	76.9	12.9	10.2	0.98
Std. Dev.	0.43	1.03	4.48	0.03	0.97	0.72	1.66	0.59	1.22	3.06	6.1	0.2	2.7	0.9	2.1	2.8	4.4	0.5	0.087	0.003	7.1	5.0	2.23	0.52
No. Samples	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	3	3	5	4	4	4	4
d/s Camrose Cr.																								
Min	5.28	11.60	27.2	0.18	6.90	2.65	5.34	1.14	5.68	17.62	66.4	0	0	6.6	15.5	15.2	23.7	4.1	0.152	0.008	17.6	22.2	19.2	1.52
Max	8.77	16.16	41.07	0.27	10.36	33.54	17.35	14.32	9.27	23.42	83.3	0.5	9	8.6	28.1	43.2	37.7	6.4	0.304	0.020	58.6	46.2	36.2	3.80
Mean	6.78	13.53	33.00	0.21	8.41	8.53	9.45	4.36	7.49	20.02	71.6	0.2	5.2	7.6	20.0	23.6	30.3	4.9	0.211	0.013	33.9	36.4	29.7	2.76
Std. Dev.	1.21	1.63	4.75	0.03	1.23	11.19	3.73	4.54	1.30	1.92	6.1	0.2	3.8	0.7	4.2	9.3	4.7	0.9	0.062	0.005	15.2	8.8	6.4	0.95
No. Samples	6	6	6	6	6	6	6	6	6	6	6	6	6	6	6	6	6	4	4	6	4	4	4	4
Hwy. 872																								
Min	1.97	3.21	12.23	0.05	4.77	2.88	4.20	0.55	0.17	5.40	33.9	0	4	5.4	9.3	8.4	15.4	6.1	0.059	0.003	87.6	3.2	6.2	0.60
Max	3.92	6.59	25.28	0.10	11.64	6.43	20.81	14.14	5.60	10.53	57.0	0	10	10.4	33.7	45.9	22.7	11.7	0.173	0.006	90.6	5	7.2	1.21
Mean	2.81	4.99	17.48	0.06	6.72	3.99	8.60	3.75	3.16	8.07	43.9		7	7.2	16.9	19.7	19.7	8.2	0.108	0.004	88.9	4.2	6.9	0.67
Std. Dev.	0.89	1.43	4.40	0.02	2.52	1.34	6.26	5.24	1.78	2.07	7.9		1.9	1.8	8.9	14.2	2.8	2.4	0.048	0.001	1.10	0.6	0.4	0.32
No. Samples	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	3	3	5	4	4	4	4
Unwin																								
Min	0.57	1.16	7.83	0	2.16	1.76	3.19	0.07	1.43	2.09	19.5	0	0	3.6	6.8	6.6	12.3	3.2	0.013	0	78.6	1.2	3.2	0.03
Max	0.81	1.97	10.05	0.06	3.11	2.39	6.26	5.40	2.03	2.92	23.6	0	3	4.4	9.9	14.0	16.1	4	0.032	0.007	95.6	11.2	10.2	0.44
Mean	0.72	1.53	8.74	0.02	2.52	2.06	4.23	1.90	1.69	2.54	22.0		2	4.0	8.2	9.1	13.6	3.5	0.023	0.003	90.6	3.9	5.5	0.14
Std. Dev.	0.09	0.28	0.84	0.02	0.31	0.22	1.04	1.90	0.21	0.26	1.4		1.0	0.3	0.9	2.6	1.4	0.3	0.007	0.002	7.1	4.2	2.9	0.20
No. Samples	6	6	6	6	6	6	6	6	6	6	6	6	6	6	6	6	6	4	4	6	4	4	4	4
Mouth																								
Min	1.16	2.53	8.89	0	3.06	1.73	3.09	0.83	1.94	4.31	27.6	0	0	4.4	9.7	10.5	18.0	5.3	0.061	0	88.6	0.1	3.2	0.03
Max	5.76	7.90	24.02	0.10	12.15	7.59	13.54	3.37	9.92	13.73	59.7	0	9	12.7	28.3	29.4	32.3	26.0	0.106	0.006	96.6	6.2	5.2	0.17
Mean	3.28	5.72	16.65	0.06	5.94	3.89	7.26	1.80	4.93	9.69	43.9		5	7.6	17.5	18.8	25.0	14.0	0.089	0.002	93.9	1.7	4.5	0.08
Std. Dev.	1.60	1.90	4.87	0.34	3.26	1.96	3.42	0.94	2.25	3.55	11.0		3.5	2.8	6.3	7.8	4.8	8.8	0.020	0.003	3.1	2.6	0.8	0.07
No. Samples	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	3	3	5	4	4	4	4

Table 3.9 Continued

	ANALYSES ON SAMPLE FRACTION < 180 µm																TOTAL						
	0.5N HCl									Aqua Regia							H_2SO_4-HNO_3			Particle Size Distribution and % C			
	%LOI	Cu	Zn	Cd	Pb	Co	Ni	Cr	V	Cu	Zn	Cd	Pb	Co	Ni	Cr	V	As	Se	Hg	% Sand	% Silt	% Clay	% C
B. HORIZONTAL DISTRIBUTION																								
d/s Camrose Cr.																								
Min	4.76	10.45	30.36	0.12	6.84	3.64	7.33	1.74	6.44	14.32	58.4	0	3	7.0	14.7	14.8	25.9	3	0.145	0.012				
Max	8.77	17.21	42.63	0.38	12.36	4.36	9.82	2.31	9.24	24.27	84.2	0.4	9	8.6	21.9	22.2	37.7	4.7	0.210	0.023				
Mean	7.18	14.97	39.32	0.28	9.65	4.05	8.9	2.12	8.49	21.12	75.8	0.1	4.8	7.9	19.2	17.8	30.7	4.9	0.179	0.017				
Std. Dev.	1.09	2.07	3.71	0.07	1.38	0.23	0.75	0.16	0.80	3.08	7.9	0.2	1.9	0.5	2.1	2.4	4.0	0.5	0.022	0.004				
No. Samples	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10				
Unwin																								
Min	0.29	0.89	7.13	0	1.40	1.75	5.46	1.15	1.22	1.38	15.6	0	2	3	10.8	7.8	8.2	2.0	0.017	0.006				
Max	1.67	3.07	15.16	0.08	3.49	3.85	15.78	24.44	3.51	4.94	33.4	0	3	5.9	16.7	26.7	16.7	10.6	0.061	0.010				
Mean	0.84	1.95	10.98	0.01	2.60	2.68	8.06	6.95	2.27	3.24	25.1	0	2	4.6	12.8	14.8	12.8	4.8	0.039	0.007				
Std. Dev.	0.55	3.06	0.03	0.77	0.73	2.91	6.98	0.82	0.58	6.90			1.1	2.1	6.6	2.9	2.3	0.2	0.001	0.001				
No. Samples	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10				
C. VERTICAL DISTRIBUTION																								
Camrose																								
Min	5.73	13.87	11.20	0.20	9.80	3.70	8.54	1.95	8.08	19.59	71.30	0	2	7.9	18.0	17.4	30.0	3.7	0.117	0.011				
Max	7.56	16.87	44.78	0.26	11.04	4.72	52.54	78.50	9.71	22.45	78.7	0.1	6	9.3	84.3	162.0	36.8	4.0	0.190	0.025				
Mean	6.46	15.23	33.81	0.23	10.18	4.05	22.20	24.02	9.00	20.92	74.5	0.1	4	8.4	38.0	60.4	32.1	3.8	0.130	0.02				
Std. Dev.	0.72	1.51	13.22	0.03	0.51	0.40	17.66	31.56	0.68	1.33	3.2	0.2	1.4	0.5	26.9	58.9	2.7	0.1	0.069	0.005				
No. Samples	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4				
Unwin																								
Min	0.66	1.28	9.26	0	2.34	2.21	3.68	0.69	1.77	2.91	23.0	0	1	4.1	7.6	5.4	11.0	3.0	0.03	0.005				
Max	1.45	3.47	16.73	0.03	4.42	3.95	18.98	23.31	4.28	9.25	38.2	0	2	7.0	29.9	52.5	25.7	6.7	0.062	0.007				
Mean	0.96	2.195	11.87	0.01	3.08	2.93	11.01	10.39	2.77	5.37	27.1	0	2	5.1	19.4	29.9	16.0	4.4	0.042	0.006				
Std. Dev.	0.30	0.82	2.91	0.01	0.82	0.64	5.91	9.37	0.93	2.53	6.3	0	0.4	1.1	8.6	19.0	5.7	1.4	0.012	0.001				
No. Samples	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4				
D. LAKES (JUNE 1989)																								
Battle Lake	3.55	4.72	22.81	0.11	2.26	1.97	5.85	3.19	5.41	7.79	48.3	<0.7	<4	7.3	19.4	21.4	25.1	3.6	0.108	0.006				
Driedmeat Lake	10.09	16.01	38.97	0.27	9.34	3.22	7.88	1.74	8.43	23.27	76.2	0.4	7	7.6	17.1	16.6	28.4	4.2	0.211	0.012				
Forestburg Res.	7.89	35.55	38.26	0.21	8.14	3.80	10.21	1.91	8.99	44.89	68.3	0.3	6	8.2	20.0	15.7	21.2	5.7	0.207	0.012				
E. SUSPENDED SEDIMENTS (APRIL 1990) COMPARED TO RIVER BOTTOM SEDIMENTS (APRIL 1990)																								
																					Sample Fraction <180 µm			
Susp. Sediment																								
Hwy 611	27.96	18.56	58.14	0.43	9.65	4.01	11.40	4.37	9.89	32.28	115.5	<0.7	<4	9.2	30.7	36.2	43.3	8.1	0.782	0.013	97.8			
d/s Camrose	14.28	20.18	45.47	0.38	11.34	4.87	15.71	11.07	8.67	31.71	102.5	<0.7	<4	10.5	35.2	48.9	44.0	7.8	0.374	0.016	95.4			
Unwin	4.83	13.41	27.39	0.10	8.81	6.07	14.74	3.72	7.01	21.89	72.7	<0.7	<4	11.0	37.5	46.5	32.3	9.8	0.209	0.023	82.4			
Bottom Sediment																								
Hwy 611	12.11	8.54	37.34	0.21	3.14	3.54	22.41	23.95	7.59	14.64	68.1	<0.7	<4	8.2	36.3	55.5	28.5	3.4	0.548	0.015	85.7			
d/s Camrose	5.28	11.60	31.71	0.18	7.86	4.21	17.35	14.32	7.07	17.62	66.4	<0.7	<4	8.6	28.1	43.2	33.6	5.0	0.230	0.019	53.1			
Unwin	0.57	1.32	8.39	<.07	2.16	1.88	6.26	5.40	1.63	2.36	21.5	<0.7	<4	3.8	9.9	14.0	16.1	3.2	0.025	0.004	81.6			

Mercury concentrations are for wet samples, all other metal concentrations are for dry samples.
Clay < 0.004 mm; silt < 0.004-0.062 mm; sand < 0.062-2.000 mm

Some of the corrections for grain size proposed by Forstner and Wittman (1981) were applied to our sediment samples (i.e. standardizing by sieving sediment; extraction of non-residual metals with dilute acids). However, no corrections are available for discrepancies in sediment organic content. The influence of the organic content (as %LOI on sieved samples) on metal concentrations in Battle River sediment was reflected in strong positive correlations with all metals (Pearson correlation on log-transformed data; $p < 0.05$). Likely as a result of the use of corrections for particle size distribution, correlations between silt or sand content in the original sample and metal levels were not significant (Pb, Co, Ni, and V) or weaker (Cu, Cd, As, Se, and Hg) than those between organic matter and metal levels.

3.3.2.1 Longitudinal Trends

Figures 3.6 to 3.10 summarize longitudinal and seasonal changes recorded in silt content, organic content and metal levels of Battle River sediments. These figures also present the results of lake sediment analyses. Each figure represents results obtained with the two extraction techniques (0.5N HCl and Aqua Regia) except Pb and Cd, for which hot extraction in Aqua Regia did not yield reliable data.

A. Battle River Sediment

Considering the dependence of metal levels on sediment characteristics, and the variation in sediment type among Battle River sites (Figure 3.6), it was expected that longitudinal patterns in metal levels would be primarily explained by changes in sediment characteristics.

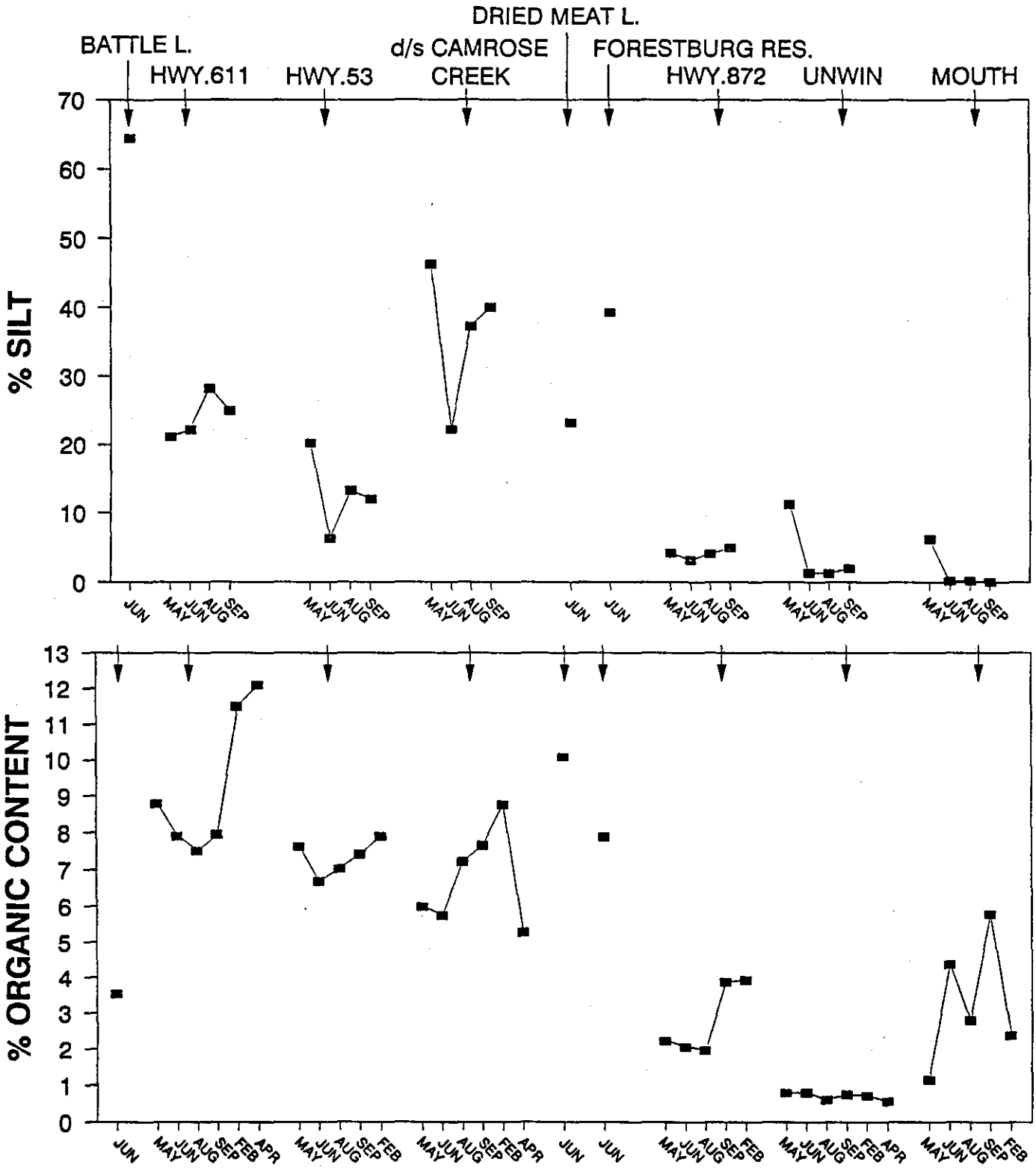

Figure 3.6 SILT CONTENT AND ORGANIC CONTENT (AS LOI ON FRACTION < 180 um) OF BATTLE RIVER SEDIMENT

MAY 1989-APR 1990

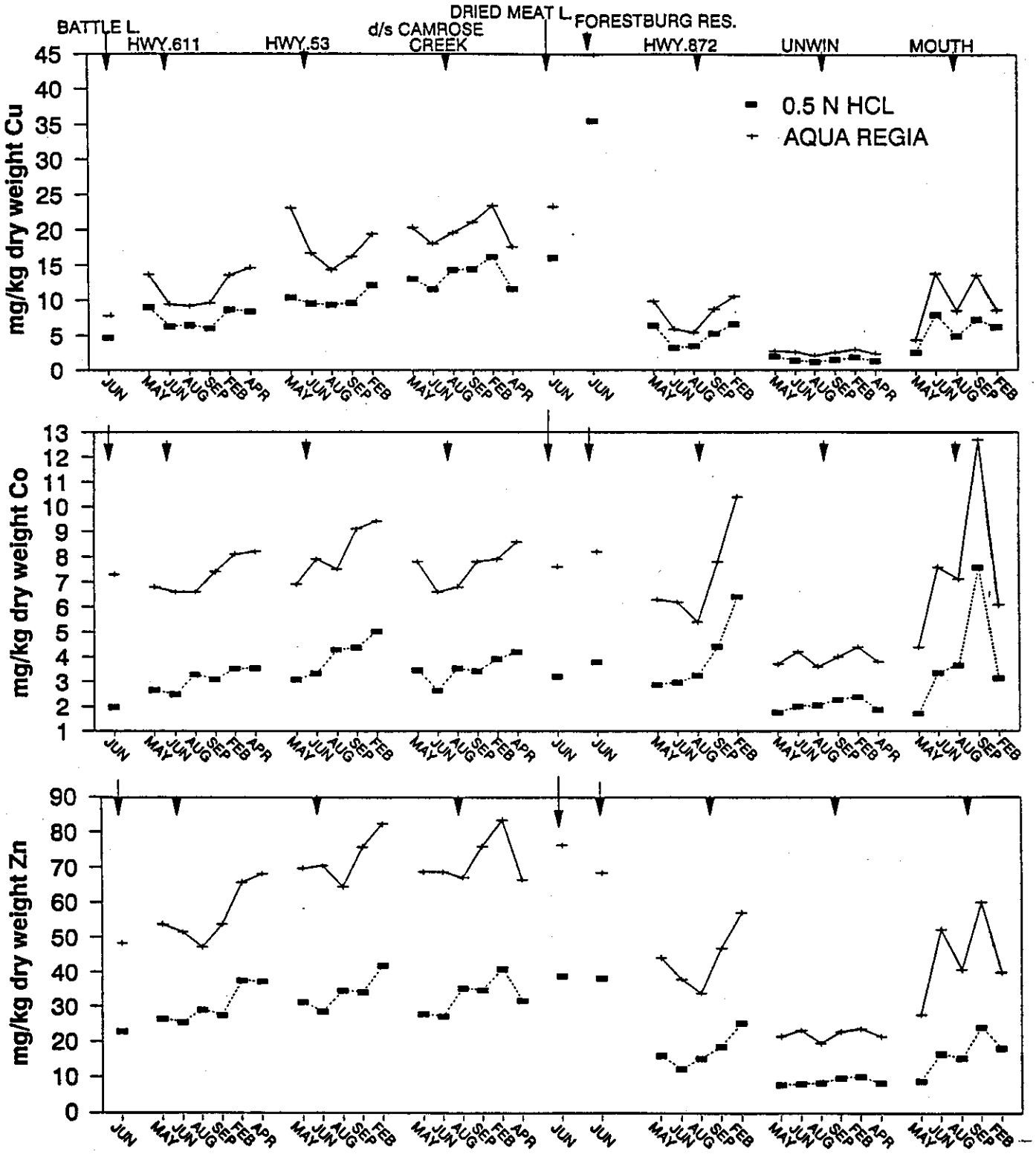

Figure 3.7 NON-RESIDUAL ZINC COBALT AND COPPER LEVELS IN BATTLE RIVER SEDIMENT (MEASURED FRACTION < 180 um)

MAY 1989-APR 1990

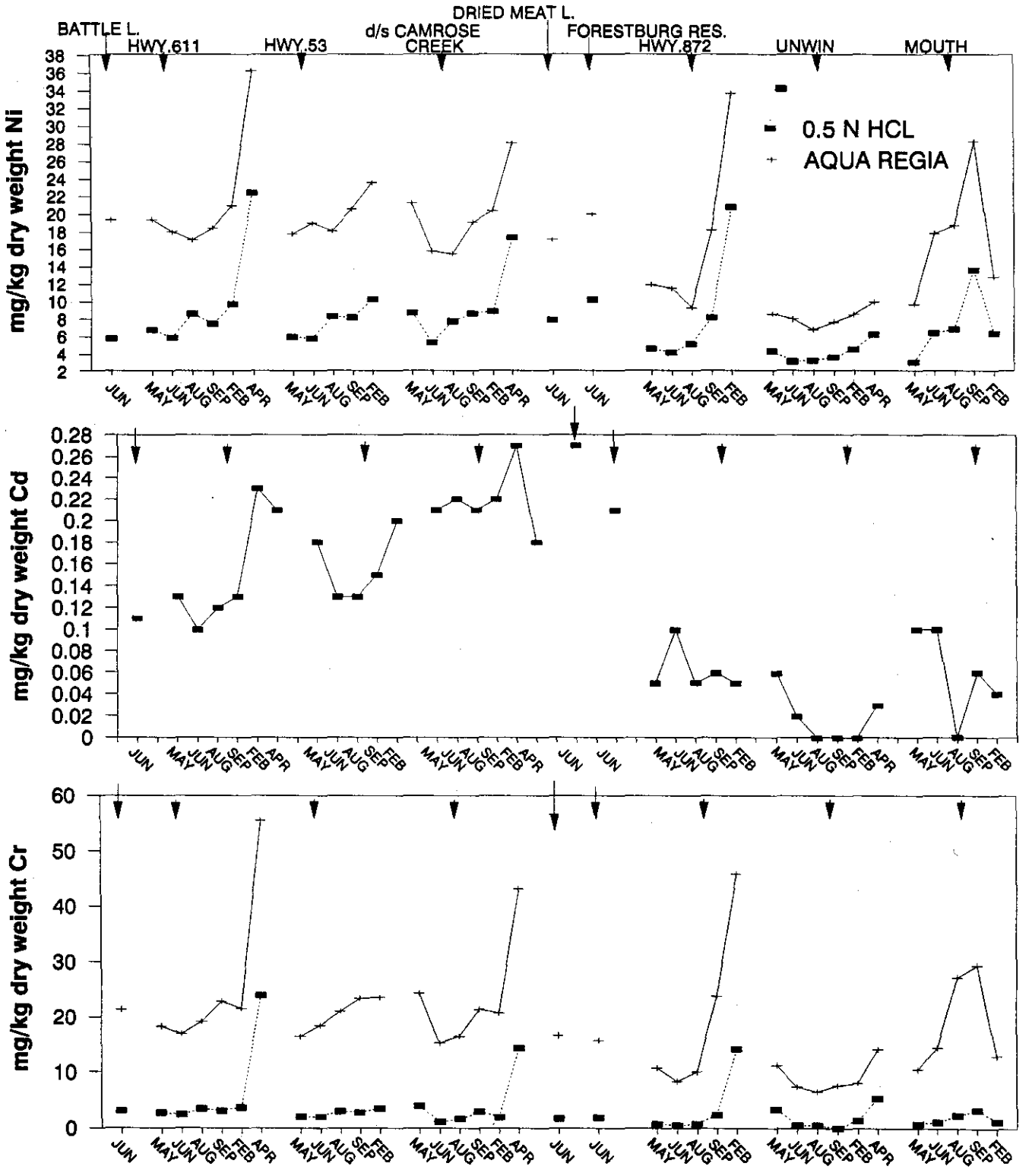

Figure 3.8 NON-RESIDUAL CHROMIUM, CADMIUM, AND NICKEL LEVELS IN BATTLE RIVER SEDIMENT (MEASURED FRACTION < 180 um) MAY 1989-APR 1990

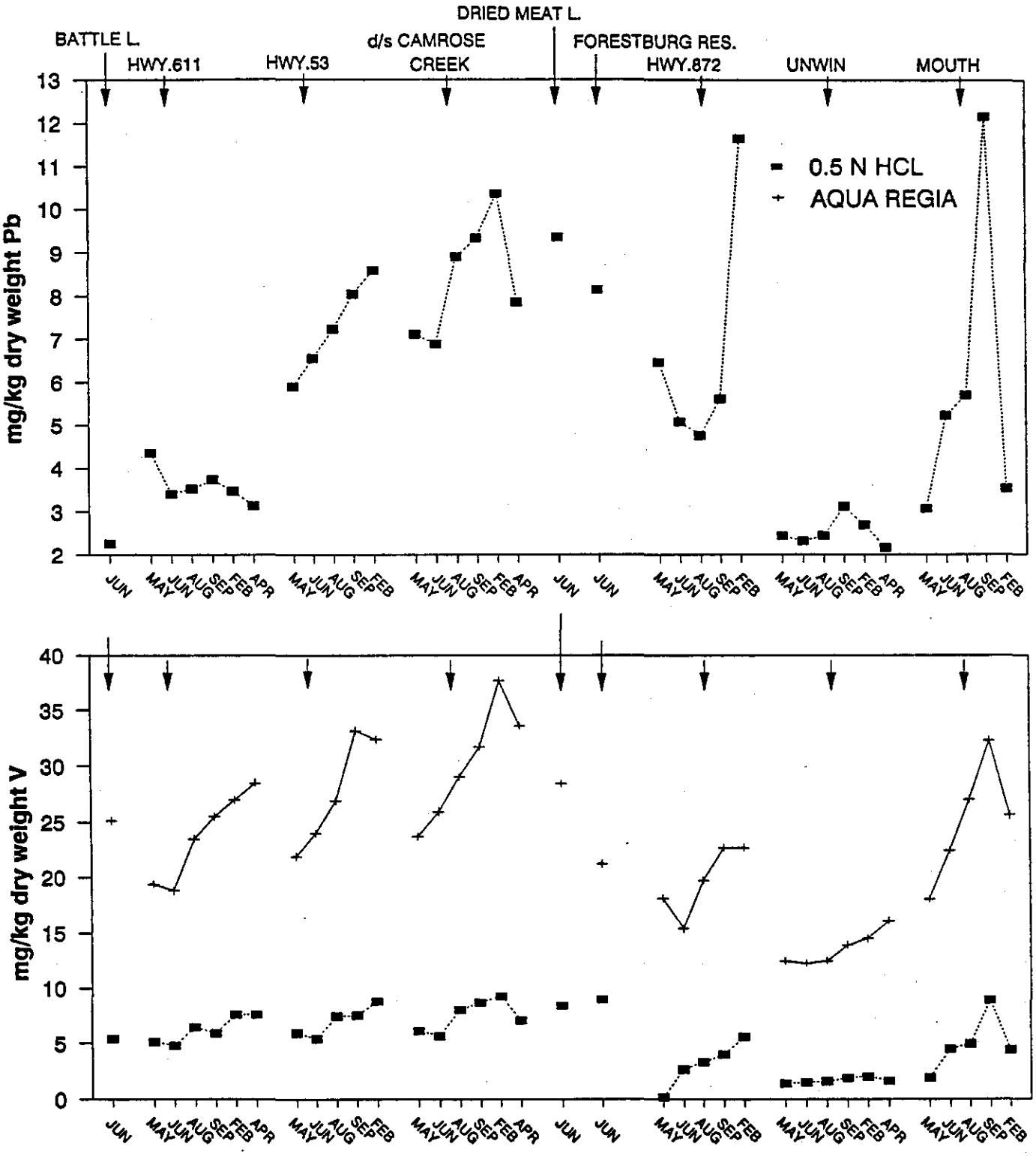

Figure 3.9 NON-RESIDUAL VANADIUM, AND LEAD LEVELS IN BATTLE RIVER SEDIMENT (MEASURED FRACTION < 180 um)

MAY 1989-APR 1990

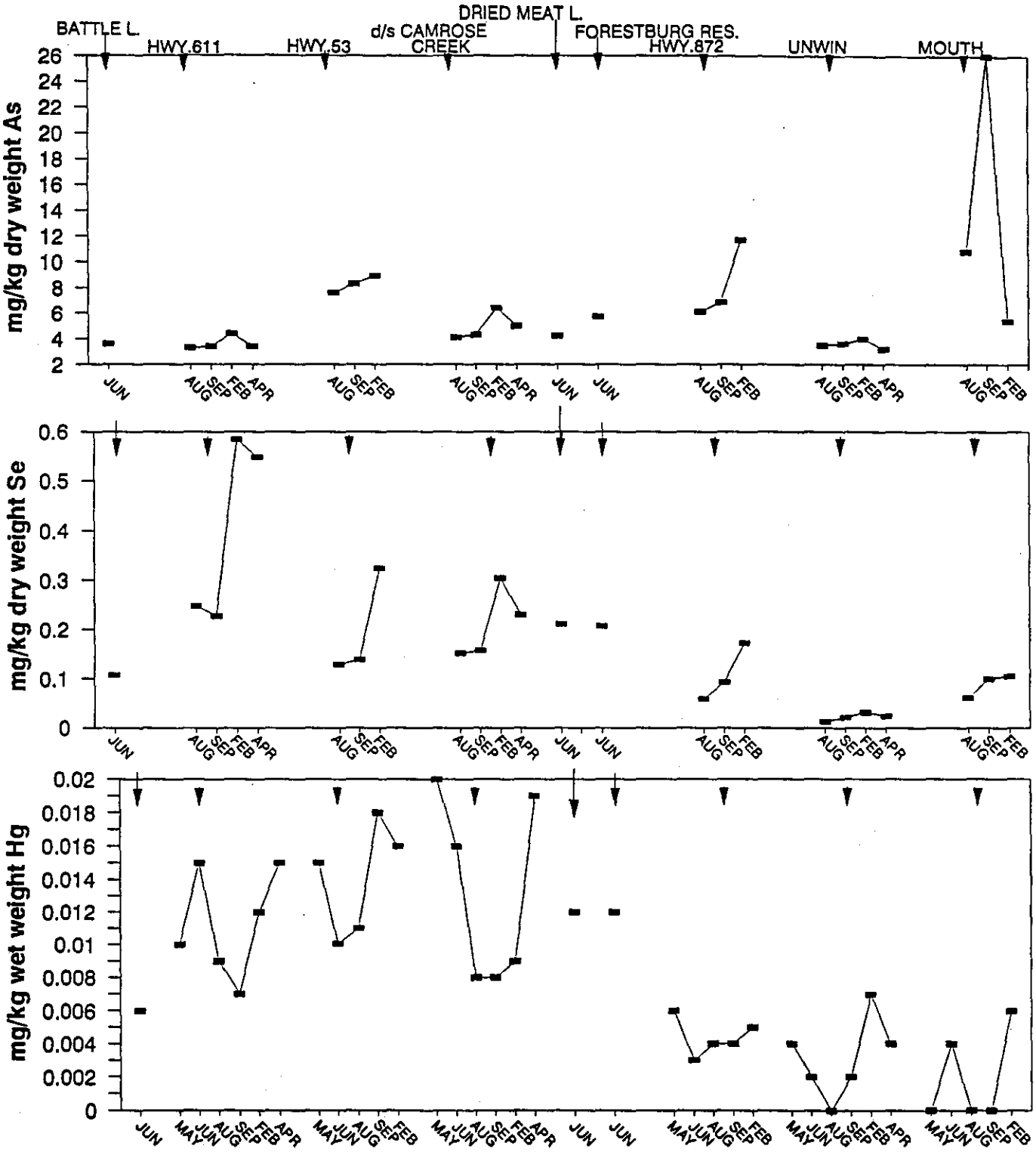

Figure 3.10 TOTAL ARSENIC, SELENIUM, AND MERCURY IN BATTLE RIVER SEDIMENT (As and Se MEASURED ON FRACTION < 180 um, EXPRESSED AS DRY WEIGHT;Hg MEASURED ON TOTAL SAMPLE, EXPRESSED AS WET WEIGHT) MAY 1989-APR 1990

The statistical significance of differences in sediment characteristics and metal levels among sites was tested with an analysis of variance (Zar 1974); the Student-Newman-Keuls test (Zar 1974) was used to compare longitudinal changes among successive pairs of sites. Results are summarized in Table 3.10. The three upper sites had similar levels of organic matter and these levels were significantly higher than those of the three lower sites. Unwin sediments had the lowest organic content and silt concentration of all sites. Corresponding to sediment characteristics, Cu, Zn, Cd, V and Hg levels were significantly higher at the three upper sites than at the lower sites, and Unwin had the lowest levels of Cu, Zn, Cd, Pb, Co, Ni and Se. For some metals such as Pb, Cu, Zn, and As, longitudinal patterns did not entirely match those of sediment characteristics. For example, Pb levels were highest at Hwy 53, d/s Camrose, at Hwy 872 and near the mouth (Table 3.9, Figure 3.9). The high Pb levels at these sites may reflect the inputs from wastewater discharges and fossil fuel burning (coal-fired power plant, leaded gasoline). The increase in Cu and Zn levels from Hwy 611 to the site d/s of Camrose Creek may also reflect anthropogenic influences. Sediment As levels only increased at the mouth, a pattern which contrasts with the well defined longitudinal trends observed in water (Section 3.2.1.2) or plant tissue (Section 3.2.4.2).

B. Lake Sediments

Sediment samples from Battle Lake, Driedmeat Lake, and the Forestburg Reservoir had similar characteristics to the sediments sampled in the Battle River at the three upper sites (Table 3.9). Metal levels

Table 3.10 Comparison of Mean Metal Concentrations Among Sediments from Six Battle River Sites Based on Results of Student-Newman-Keuls Test (values in mg/kg unless otherwise stated).

	Hwy 611		Hwy 53		d/s Camrose Creek		Hwy 872		Unwin		Near Mouth
Sediment Characteristics											
organic content (LOI)(%)	9.30	=	7.33	=	6.78	>	2.81	>	0.71	<	3.28
silt portion (%)	24.2	=	12.9	=	36.4	>	4.2	>	3.9	>	1.7
HCl Extraction											
Cu	7.51	<	10.24	<	13.53	>	4.99	>	1.53	<	5.72
Zn	30.56	=	34.12	=	33.00	>	17.48	>	8.74	<	16.65
Cd	0.15	=	0.16	=	0.21	>	0.06	>	0.02	<	0.06
Pb	3.61	<	7.27	=	8.41	=	6.72	>	2.52	<	5.94
Co	3.10	=	4.02	=	8.53	=	3.99	>	2.06	<	3.89
Ni	10.19	=	7.74	=	9.45	=	8.60	>	4.23	<	7.26
Cr	6.61	=	2.74	=	4.36	=	3.75	=	1.90	=	1.80
V	6.25	=	7.03	=	7.49	>	3.16	=	1.69	=	4.93
Aqua Regia Extraction											
Cu	11.72	<	17.95	<	20.02	>	8.07	>	2.54	<	9.69
Zn	56.7	<	72.5	=	71.6	>	43.9	>	22.0	<	43.9
Co	7.3	=	8.2	=	7.6	=	7.2	>	4.0	<	7.6
Ni	21.7	=	19.8	=	20.0	=	16.9	>	8.2	<	17.5
Cr	25.7	=	20.6	=	23.6	=	19.7	>	9.1	<	18.8
V	23.7	=	27.7	=	30.3	>	19.7	>	13.6	<	25.0
Total											
As	3.6	=	8.3	=	4.9	=	8.2	=	3.5	<	14.0
Se	0.402	=	0.197	=	0.211	=	0.108	>	0.023	<	0.089
Hg	0.011	=	0.014	=	0.013	>	0.004	=	0.003	=	0.002

Legend

= no significant difference between means ($P<0.05$);
> significantly greater than; and
< significantly less than

in the lake sediments were also comparable to those measured in river sediments (Figure 3.7 to 3.10) with the exception of Cu levels in the Forestburg Reservoir (Figure 3.7). The Forestburg Reservoir samples had Cu levels which were at least twice as high as those of any other sediment samples collected in the basin. The reason for these elevated levels is not clear. Copper based biocides, commonly used to control bacterial and algal growth in cooling towers, are not used presently by the Alberta Power Ltd. plant. The only potential copper source from this operation is a boiler made of copper alloy which is cleaned every 3 to 5 years (pers. comm. C.Ng, Standards and Approvals Division). Additional sampling of the Forestburg Reservoir sediment and the boiler wastewater are required to confirm the high Cu levels.

3.3.2.2 Seasonal and Horizontal Variability

Although metal levels vary over time, the changes may be due more to sediment characteristics and spatial heterogeneity than actual seasonal changes. As discussed earlier, differences in sediment characteristics explain a large portion of inter-site variability. A comparison of temporal changes in sediment characteristics (Figure 3.6) with temporal changes in metal levels (Figure 3.7 to 3.10) suggests that sediment type may also account for the perceived temporal variability in metal levels.

The extent of horizontal variability in sediment metal levels was explored d/s of Camrose Creek and at Unwin. Descriptive statistics of samples collected at both sites are presented in Table 3.9. An F-test (Zar 1974) on log-transformed data was used to compare seasonal and

horizontal variability at these two sites. For most metals there was no significant difference in the variance of samples describing horizontal or temporal metal distribution (Table 3.11). Exceptions were Zn, Pb, Co, and V (extraction in 0.5N HCl) and Cu, Zn, and Co (Aqua Regia extraction) at Unwin where variability was more horizontal than temporal. Even though seasonal variability may exist in sediment metal residue levels in the Battle River, it tends to be similar or smaller in magnitude to spatial (intra-site) variability and cannot be distinguished from the latter. That is to say, apparent differences over time may simply result from the patchiness (spatial variability) of sediment quality at a site.

3.3.2.3 Vertical Variability

Vertical distribution of metal levels at different sediment depths was explored at the site downstream of Camrose Creek and at Unwin. Descriptive statistics of these samples are presented in Table 3.9; detailed results are shown in Section 2. For most metals, concentration did not change with depth in a recognizable pattern, even though a relationship was apparent between the organic content of the sediment and the concentration of some metals. For most metals, the range for horizontal and vertical samples was similar (Table 3.9) and variances in the two data sets were not significantly different (Table 3.11). However, several metals had unexpectedly low or high concentrations. For example in the 0-2 cm depth zone d/s of Camrose Creek, Ni and Cr concentrations were considerably higher than in any other sample and were beyond the range of values describing the horizontal variability. Zinc levels in that sample were also unusual: Zn

Table 3.11 Summary of F-test Results: Comparison of Variance in Sediment Samples Describing Horizontal, Seasonal and Vertical Distribution of Metal Levels.

	Horizontal versus Seasonal				Horizontal versus Vertical			
	0.5 N HCl		Aqua Regia/Total		0.5 N HCl		Aqua Regia/Total	
	Camrose	Unwin	Camrose	Unwin	Camrose	Unwin	Camrose	Unwin
Cu	-	-	-	S_1	-	-	-	-
Zn	-	S_1	-	S_1	-	-	-	-
Cd	-	bd	bd	bd	-	bd	bd	bd
Pb	-	S_1	bd	bd	-	-	bd	bd
Co	-	S_1	-	S_1	-	-	-	-
Ni	-	-	-	-	-	-	-	-
Cr	-	-	-	-	-	-	-	-
V	-	S_1	-	-	-	-	-	-
As (total)			bd	bd			S_2	-
Se (total)			bd	bd			-	-
Hg (total)			bd	bd			-	-

Legend

- no significant differences between variances (P>0.05)
bd too many values below detection limit
S_1 significant difference; P>0.05; Fcal.>Ftab.=6.68, N_1=9, N_2=5
S_2 significant difference; P>0.05; Fcal.>Ftab.=14.5, N_1=9, N_2=3

extractions in 0.5N HCl yielded exceptionally low concentrations, even though Aqua Regia extractions fell within the range of expected values.

3.3.3 Suspended Sediments

Suspended sediment samples were obtained at three sites (Hwy 611, d/s Camrose Creek, and Unwin) on one occasion only. Because of the small size of the data set, the discussion of results will be limited to a comparison with sediment data collected simultaneously at these sites.

Characteristics of suspended sediments (Table 3.9) followed the same longitudinal trends as those of river bottom samples: the organic content declined in a downstream direction and the sediment became coarser (less sample material passed through a 180 μm sieve; no complete particle size analysis was done). However, suspended sediments contained more organic matter than river bottom sediments at the corresponding sites. Considering the affinity of metals for organic matter and the difference in organic levels between suspended and bottom sediment samples, one would expect metal levels in suspended sediments to be higher than in bottom sediments. This was true for all metals except Cr (0.5N HCl extraction) and two out of three Hg measurements which were higher in bottom sediments.

A comparison of longitudinal trends in suspended and bottom sediments indicates that trends in these media are not always the same and that trends in metal levels may be influenced by extraction techniques. For HCl extractions, longitudinal trends for Cu, Zn, Cd, Pb and V were similar in suspended and bottom sediments; they were different

for Co, Ni and Cr (Table 3.9). For Aqua Regia extractions, trends were similar for Zn only, but differed for Cu, Co, Ni, Cr, and V. Finally, longitudinal trends in sediments and suspended sediments were different for Hg, and As.

In a study on the Bow and Oldman rivers, Ongley (1987) examined the value of information contained in suspended sediment samples collected at different flow regimes and concluded that spring (high flow) sediment chemistry largely reflects background chemistry of the catchment soils whereas summer (low flow) sediment chemistry contains considerably more information about point-sources. Considering that suspended sediments in the Battle River were sampled only at run-off time, they would, according to Ongley, reflect background chemistry of catchment soils rather than point sources.

3.3.4 Biota

3.3.4.1 Aquatic Invertebrates

A total of 8 different invertebrate taxa were sampled for tissue analysis. Samples of Oligochaeta and Chironomidae were too small to determine moisture content. Residue levels for wet weight tissue are not comparable among taxa and results for Chironomidae and Tubificidae are not discussed here although they are included in the tables.

3.3.4.1.1 Longitudinal Trends

With the possible exception of mercury and nickel, metal levels in aquatic invertebrates showed no consistent longitudinal trends in the Battle River (Table 3.12). Mercury levels were more frequently

Table 3.12 Total Metal Concentrations in Aquatic Invertebrates Collected in 1989 at Six Sites in the Battle River (concentrations as mg/kg dry weight, Hg as wet weight)

	Cu	Zn	Ni	Cr	V	Hg	As	Se
				SPRING (JUNE) 1989				
Hwy 611								
Amphipoda	75	130	2	4	4.2	0.014	12.74	
Sphaeriidae	8.2	41	1.4	3.0	3.77	0.014	4.23	
Hirudinea	18	370	2	1.9	1.4	(0.007)	14.0	
Simuliidae	28	280	13	23.2	24.4	0.014	23.7	
Hwy 53								
Amphipoda	97	140	2	3.7	4.6	0.014	11.81	
Sphaeriidae	6.9	36	0.9	1.0	1.76	0.013	4.15	
Unionidae	7	270	<2	2.9	<0.2	0.025	14.92	
Hirudinea	42	430	<2	1.3	1.3	(0.007)	20.6	
d/s Camrose Cr.								
Amphipoda	70	110	2	4.6	7.7	0.015	13.25	
Hirudinea	17	300	1	0.9	1.1	0.026	19.55	
Chironomidae	3.0*	15*	1.9*	2.98*	5.66*	**		
Tubificidae	2.4*	10*	6.0*	13.34*	4.45*	**		
Hwy 872								
Amphipoda	83	120	4	5	8.5	(0.005)	12.86	
Sphaeriidae	4.1	14	3.4	2.7	1.48	0.008	5.12	
Unionidae	10	260	3	2.4	<0.2	0.011	7.68	
Hirudinea	30	460	2	0.7	0.9	<0.008	19.38	
Unwin								
Amphipoda	81	120	2	3.1	5.7	<0.008	8.23	
Sphaeriidae	5.0	17	1.0	0.5	1.04	<0.008	1.39	
Near Mouth								
Amphipoda	88	110	3	4.7	7.5	0.008	9.39	
Sphaeriidae	5.8	17	1.7	1.0	1.89	<0.008	4.11	
Unionidae	1.5*	41*	0.4*	0.42*	0.13*	<0.008	0.80	
				FALL (SEPTEMBER) 1989				
Hwy 611								
Amphipoda	76	90	<2	0.6	1.2	0.009	3.88	0.5
Sphaeriidae	5.9	24	0.5	0.5	0.85	(0.004)	0.62	0.2
Gastropoda	44.6	60	3.8	3.1	6.1	0.013	1.15	0.6
Hwy 53								
Amphipoda	67	80	<1	0.5	1.0	(0.005)	0.98	0.9
Sphaeriidae	8.8	23	0.8	0.5	1.06	(0.005)	0.70	0.2
Gastropoda	42.9	50	4.0	2.3	4.60	(0.004)	1.15	0.8
d/s Camrose Cr.								
Amphipoda	73	80	4	1.4	3.4	(0.006)	1.29	0.8
Gastropoda	73.8	60	6.2	3.2	7.2	0.018	2.62	0.2
Gastropoda	59.6	60	6.2	3.1	6.5	0.015	2.79	0.1
Tubificidae	2.2*	19*	1.0*	1.76*	3.4*	**	**	**
Hwy 872								
Amphipoda	83	70	2	1.5	3.2	(0.004)	3.56	0.1
Sphaeriidae	4.8	9	0.9	0.1	0.52	(0.004)	2.03	0.3
Gastropoda	41.1	38	4.8	1.9	4.7	(0.004)	2.05	0.7
Unionidae	7	310	3	4.9	0.5	(0.007)	2.86	2.5
Unionidae	11	260	11	3.3	0.9	0.009	2.89	2.7
Unwin								
Amphipoda	86	70	2	1.7	3.3	(0.006)	2.96	0.2
Sphaeriidae	8.1	15	1.1	0.1	0.44	(0.004)	0.49	0.2
Unionidae	8	370	3	3.2	(0.1)	0.011	2.85	0.2
Unionidae	6	110	2	1.2	0.8	0.010	2.80	2.2
Near Mouth								
Amphipoda	9.9*	9*	0.2*	0.15*	0.36*	(0.005)	**	**
Amphipoda	9.5*	9*	0.3*	0.16*	0.40*	(0.004)	**	**
Sphaeriidae	3.4	7	0.8	0.3	0.58	(0.004)	0.81	0.2
Unionidae	12	390	4	3.3	0.3	0.018	6.11	4.0
Unionidae	10	420	4	2.3	0.3	0.011	0.86	1.9

* insufficient sample for moisture analysis, concentration applies to wet tissue
** insufficient sample for analysis
() values in parenthesis indicate measurable concentrations below the method detection limit

above the detection limit at the three upstream sites (i.e. 60% of samples) than at the three downstream sites (i.e. 25% of samples) and nickel levels tended to be highest at the sites below Camrose Creek and at Hwy 872.

3.3.4.1.2 Seasonal Trends

Amphipods, sphaeriids and unionids were collected in May (spring) and September (fall) and these samples provide some indication of temporal variability in metal residue levels in aquatic organisms.

On average, tissue samples contained considerably more As, Cr, Zn and V in spring than in fall (Table 3.13). Such seasonal differences were also measurable at the level of individual invertebrate groups. Levels of As, Cr, and Zn residues in amphipods, sphaeriids and unionids were higher in spring than in fall. Copper levels were similar in spring and fall. Seasonal changes in Ni were inconsistent among taxa: levels were lower in fall for amphipods and sphaeriids, but higher for unionids. Mercury levels were more frequently above the detection limit in spring than in fall (70 and 30% of samples, respectively) (Table 3.13). Moore and Ramamoorthy (1984) state that invertebrate uptake of many metals is directly related to metabolic rate, hence lower temperatures generally cause a reduction in body burdens. Similarly, Wageman et al. (1978) found that As levels in aquatic invertebrates were highest at a time when water temperature was highest. Highest temperatures in the Battle River are reached in the month of July (Anderson 1991). Hence, spring samples were collected when temperatures were rising, whereas in fall they were collected when temperatures were

TABLE 3.13 Summary of Metal Levels in Aquatic Invertebrates from the Battle River in Spring and Fall, 1989
(concentrations as mg/kg dry weight, Hg as wet weight)

	Average		Amphipoda		Sphaeriidae		Unionidae		Hirudinea	Simuliidae	Gastropoda
	Spring (n=18)	Fall (n=21)	Spring (n=6) x̄(min-max)	Fall (n=5) x̄(min-max)	Spring (n=5) x̄(min-max)	Fall (n=5) x̄(min-max)	Spring (n=2) x̄(min-max)	Fall (n=6) x̄(min-max)	Spring (n=4) x̄(min-max)	Spring (n=1)	Fall (n=4) x̄(min-max)
As	11.50	2.20	11.38 (8.23-13.20)	2.53 (0.98-3.88)	3.80 (1.39-5.12)	0.93 (0.49-2.03)	11.30 (7.68-14.92)	3.06 (0.86-6.11)	18.4 (14.0-20.6)	24.4	1.95 (1.15-2.79)
Cr	3.7	1.9	4.2 (3.7-5.0)	1.1 (0.5-1.7)	1.6 (0.5-3.0)	0.3 (0.1-0.5)	2.7 (2.4-2.9)	3.0 (1.2-4.9)	1.2 (0.7-1.9)	23.2	2.7 (1.9-3.2)
Cu	37.7	34.9	82 (70-97)	77 (67-86)	6.0 (4.1-8.2)	6.2 (3.4-8.8)	9 (7-10)	9 (6-12)	27 (17-42)	28	52.4 (41.1-73.8)
Ni	3.0	3.2	3 (2-4)	2 (<1-4)	1.7 (0.9-3.4)	0.8 (0.5-1.1)	3 (<2-3)	5 (2-11)	2 (<2-2)	13	5.0 (3.8-6.2)
Se	NA	0.9	NA	0.5 (0.1-0.9)	NA	0.2 (0.2-0.3)	NA	1.6 (0.2-4.0)	NA	NA	0.5 (0.1-0.8)
V	4.6	2.3	6.4 (4.2-8.5)	2.4 (1.0-3.4)	1.99 (1.04-3.77)	0.70 (0.40-1.10)	0.2 (0.2-0.2)	0.5 (0.1-0.9)	1.2 (0.9-1.4)	24.4	5.8 (4.6-7.2)
Zn	182	124	122 (110-140)	78 (70-90)	25 (14-41)	16 (7-24)	265 (260-270)	310 (110-420)	390 (300-460)	280	54 (38-60)
Hg			(<0.010-0.010)	<0.010	(<0.010-0.010)	<0.010	<0.010-0.020	<0.010-0.020	<0.010	0.010	<0.010-0.020

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dropping. Therefore, temperature differences and the resulting difference in metabolic activity combined, with differences in population age or size distribution, may also explain the differences in body burdens observed in invertebrates from the Battle River.

3.3.4.1.3 Variability Among Duplicate Samples

Duplicate amphipod, unionid, and gastropod samples were collected in September at several locations (Table 3.14). Variability among pairs of replicate amphipod and gastropod samples was generally low for all metals, but was very inconsistent among pairs of unionid samples. Amphipod and gastropod samples were composites of at least 50 specimens each, and residue levels can be viewed as averages for the populations.

In contrast, differences in residue levels in Unionidae reflect variability among individual clams as each unionid sample consisted of the soft tissue of a single clam. The variability in residue levels among specimens could be a function of habitat variability, age, sex, or species. Many metals are concentrated in specific organs and incomplete homogenization of organ tissue may have contributed to differences in residue levels among pairs of clams.

The differences in concentrations of certain metals in pairs of clams was sometimes remarkable. For example, the range in As levels in two clams collected near the Mouth was nearly as large as the range of As levels in all invertebrate samples collected in September. However, these two clams had identical Ni levels and comparable residue levels of Cr, Cu and Zn (Table 3.14). The degree of variability in metal residue

Table 3.14 Metal Residue Levels in Duplicate Aquatic Invertebrate Samples from the Battle River (Fall 1989)

	Amphipoda[1]	Unionidae[2]			Gastropoda[2]
	Mouth	Hwy 872	Unwin	Mouth	d/s Camrose Cr.
As	-	2.86-2.89	2.80-2.85	0.86-6.11	2.62- 2.79
Cr	0.15-0.16	3.3-4.9	1.2-3.2	2.3-3.3	3.1-3.2
Cu	9.5-9.9	7-11	6-8	10-12	59.6-73.8
Ni	0.2-0.3	3-11	2-3	4-4	6.2-6.2
Se	-	2.5-2.7	0.2-2.2	1.9-4.0	0.1-0.2
V	0.36-0.40	<0.5-0.9	(0.1)-0.8	<0.3-<0.3	6.5-7.2
Zn	9-9	260-310	110-370	390-420	60-60
Hg[1]	(0.004)-(0.005)	(0.007)-0.009	0.010-0.011	0.011-0.018	0.015-0.018

[1] mg/kg wet weight (not enough sample to measure moisture content)
[2] mg/kg dry weight
() values in parenthesis indicate measurable concentrations below the method detection limit

levels in large clams from the Battle River is not unusual. Wageman et al. (1978) examined the variability in individual As levels in a variety of aquatic organisms and found that for many taxa individual variability exceeded analytical variability.

3.3.4.1.4 Variability Among Invertebrate Taxa

Considerable differences in metal residue levels were found among different taxa (Table 3.12). The simuliid (blackfly) sample collected in May at Hwy 611 had levels of As, Cr, Ni, V and Zn which were higher than any other invertebrate taxon. Blackfly larvae are filter-feeders which derive their food from small particles suspended in the water. Unlike other invertebrate groups sampled in the Battle River, these larvae had little contact with bottom sediments and most of their metal content is likely derived from the water column. Hirudinea had high levels of Zn and As, whereas Cu residues in amphipods and gastropods were considerably higher than in other invertebrate samples. Unionidae contained the highest levels of Se.

Sphaeriidae are notable because of their low levels of As, Cu, Cr, and Zn. For practical reasons (i.e. small size), sphaeriid samples consisted of both shells and soft tissue, whereas unionid clams consisted of soft tissue only. Zinc and other metals are known to concentrate in mollusc organs rather than shells (Moore and Ramamoorthy 1984, Jordao and Nickless 1989). Exclusion of shells in unionid analyses would have resulted in higher relative metal levels than if shells had been included. In the Battle River, molluscs which were analysed without shells (unionids) had higher levels of Zn than molluscs which were

analysed in their entirety (sphaeriids, gastropods) (Table 3.13). The distribution of As among molluscs also suggests concentration in organs rather than in shells. However, high levels of Cu and Cr in gastropods relative to sphaeriids suggest that different groups of organisms concentrate metals at different rates.

3.3.4.2 Aquatic Plants

Plant tissues for analysis consisted of two types of macrophyte tissue (stem and leaf samples of Potamogeton richardsonii, roots or rhizomes of this macrophyte), and filamentous green algae (Table 3.15).

3.3.4.2.1 Longitudinal Trends

Longitudinal trends in metal residue levels differed considerably among the three plant-tissue groups. They were generally most consistent for stems and leaves and corresponded well to those defined in water. Marine macro-algae are believed to time-integrate metal concentrations in water (Phillips 1980). The similarity between trends in water and in stems and leaves in the Battle River suggests that macrophytes may behave similarly to their marine counterparts and could be used as integrators of ambient concentrations over the growing season. Although residue levels of some metals (V and As) increased progressively from Hwy 611 to the Mouth, residue levels for most other metals (Cu, Zn, Ni, Cr, Se) were considerably higher in samples from the three lower sites than in samples from the three upper sites (Table 3.16, Figure 3.11). Mercury levels were below the detection level at all but one (Hwy 611) site and this element was the only one without an identifiable trend.

Table 3.15 Total Metal Residue Levels in Aquatic Plants, August 1989
(concentration as mg/kg dry weight, Hg as wet weight)

	Cu	Zn	Ni	Cr	V	As	Se	Hg
Hwy. 611								
P. richardsonii								
stems & leaves	1.9	8.3	1.8	0.7	0.11	0.94	0.09	0.058
rhizome	14.0	59.6	16.5	30.2	43.05	7.74	0.53	(0.007)
Filamentous green algae	9.7	42.7	7.7	8.6	11.22	1.69	0.21	<0.010
Hwy. 53								
P. richardsonii								
stems & leaves	2.6	17.1	1.8	1.2	1.28	0.95	0.09	<0.010
rhizome	5.2	33.2	6.3	11.7	21.13	28.27	0.16	(0.004)
Filamentous green algae	2.8	19.5	2.3	3.8	6.28	1.34	0.09	<0.010
d/s Camrose Cr.								
P. richardsonii								
stems & leaves	1.8	10.8	3.3	0.5	1.56	1.19	0.09	<0.010
rhizome	4.6	24.2	3.5	5.7	14.02	40.96	0.07	<0.010
Filamentous green algae	4.3	11.1	6.0	2.6	4.18	6.16	0.20	(0.005)
Hwy. 872								
P. richardsonii								
stems & leaves	7.6	38.0	9.6	3.1	5.11	2.14	0.24	<0.010
rhizome	8.4	38.3	9.3	12.2	31.56	243.19	0.17	<0.010
Filamentous green algae	2.8	12.7	2.9	3.9	7.49	1.09	0.19	<0.010
Unwin								
P. richardsonii								
stems & leaves	5.7	20.6	7.8	3.6	7.99	3.54	0.32	<0.010
rhizome	3.9	18.0	3.7	4.5	11.96	224.57	0.07	<0.010
Filamentous green algae	5.3	15.6	9.2	5.0	10.08	25.29	0.24	<0.010
Near Mouth								
P. richardsonii								
stems & leaves	6.6	18.6	9.2	4.5	9.90	2.22	0.30	<0.010
rhizome	14.9	32.1	8.3	9.6	18.75	**	**	**

** not enough sample material
() values in parenthesis indicate measurable concentrations below the method detection limit

Table 3.17 Total Metal Concentration (mg/kg) in Fish Muscle Tissue from the Forestburg Reservoir, November 1989.

	Cu		Zn		Ni		Cr		V		Hg		As		Se	
	wet	dry	wet	dry	wet	dry	wet	dry	wet	dry	wet	dry	wet	dry	wet	dry
White Sucker																
#1 male 43.0 cm	0.6	2.6	3	13	<0.2	<0.9	0.10	0.4	0.02	0.09	0.246	1.06	<0.007	<0.03	(0.06)	0.3
#2 male 36.4 cm	0.4	1.9	4	19	<0.2	<1.0	0.15	0.7	0.03	0.14	0.169	0.81	<0.007	<0.03	(0.04)	(0.2)
#3 female 45.0 cm	0.4	2.0	4	20	<0.2	<1.0	0.11	0.5	0.02	0.10	0.167	0.83	<0.007	<0.03	(0.06)	0.3
#4 female 41.7 cm	0.5	2.2	4	18	<0.2	<0.9	0.10	0.4	0.02	0.09	0.112	0.50	<0.007	0.03	(0.02)	(0.1)
#5 male 34.7 cm	0.4	1.8	4	18	<0.2	<0.9	0.14	0.6	0.02	0.09	0.104	0.46	<0.031	0.14	0.08	0.4
Northern Pike																
#1 female 57.4 cm	0.2	0.9	4	18	<0.2	<0.9	0.12	0.5	0.02	0.09	0.219	1.00	<0.007	<0.03	(0.06)	0.3
#2 male 45.9 cm	0.2	0.9	5	22	<0.2	<0.9	0.11	0.5	0.03	0.13	0.232	1.03	<0.007	<0.03	0.09	0.4
#3 male 54.9 cm	0.2	0.9	5	23	<0.2	<0.9	0.12	0.6	0.03	0.14	0.341	1.57	<0.007	<0.03	0.08	0.4
#4 male 36.2 cm	0.3	1.4	4	19	<0.2	<0.9	0.10	0.5	0.03	0.14	0.144	0.67	0.013	0.06	0.08	0.4
#5 male 46.2 cm	0.3	1.3	4	17	<0.2	<0.9	0.10	0.4	0.02	0.09	0.225	0.97	0.023	0.10	0.07	0.3
#6 female 36.3 cm	0.2	0.9	5	23	<0.2	<0.9	0.11	0.5	0.02	0.09	0.106	0.50	0.019	0.09	0.08	0.4
#7 female 36.3 cm	0.2	0.9	6	28	<0.2	<0.9	0.11	0.5	0.02	0.09	0.103	0.48	0.010	0.05	<0.07	<0.3

() values in parenthesis indicate measurable concentrations below the method detection limit

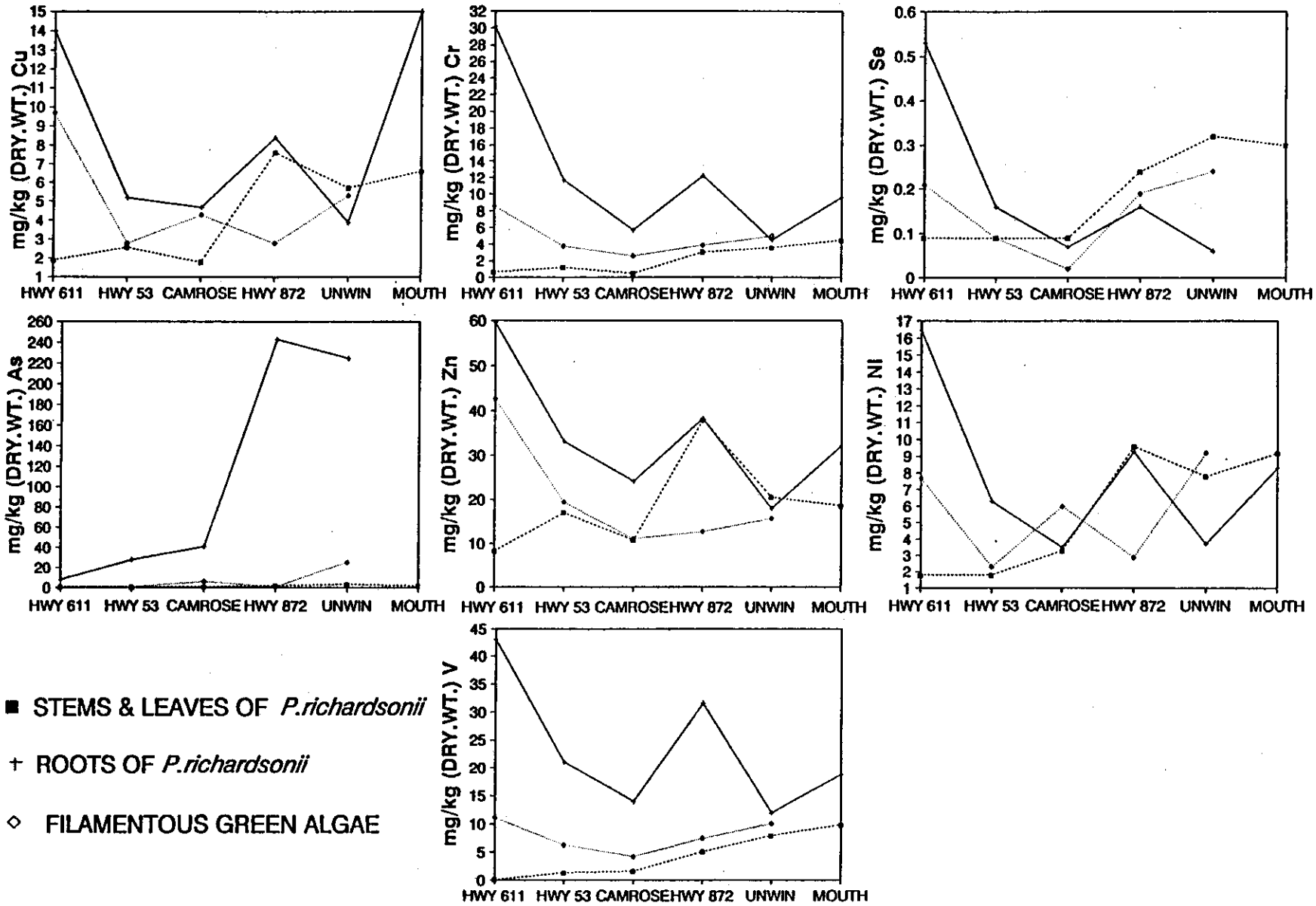

Figure 3.11 TOTAL METAL LEVELS IN PLANT TISSUE FROM THE BATTLE RIVER AUGUST 1989

In general, longitudinal trends in rhizomes of P. richardsonii were unrelated to trends apparent in stems and leaves. Although mean Cu levels were higher at the lower three sites, most metals (Cr, Ni, Se, V, and Zn) had mean residue levels which were higher at the three upper sites and in particular at Hwy 611 (Table 3.16, Figure 3.11). In both cases, the concentration ranges overlapped greatly. The exception was As in root tissue which showed a pronounced increase in a downstream direction (Table 3.16, Figure 3.11). Mercury levels were consistently below the detection level.

The large site-to-site variability of metal levels in filamentous algae did not permit an assessment of longitudinal trends. Similarly to P. richardsonii root samples, filamentous algae at Hwy 611 contained higher metal levels than at most other sites.

3.3.4.2.2 Variability Among Plant Tissue Samples

There were considerable differences among metal levels in the three types of plant tissues. Root samples usually contained higher metal levels than stems and leaves, whereas in filamentous green algae metal levels were intermediate to macrophyte root and stem-and-leaf samples (Table 3.16). Most exceptions to this pattern occurred at the three downstream sites. In the Oldman River, Blatchford and Ongley (1984) also reported consistently higher metal concentrations in filamentous algae than in Potamogeton spp.

3.3.4.3 Fish

White sucker and pike samples were collected on one occasion from the Forestburg Reservoir for metal analysis.

Levels of Ni, Cr, V and As were generally below the detection level in muscle tissue from both fish species; only Cu, Zn, Hg and Se occurred at measurable levels. Cu levels in white sucker were consistently higher than in pike (Table 3.17), but mean Zn, Hg and Se levels were not significantly higher in pike than white sucker (t-test on log-transformed data, $df = 10$, $p < 0.05$).

Intra-specific variability of metal levels was generally low. In both species the greatest degree of variability was encountered for Se, Hg and Zn levels.

The use of a metal knife on pike sample #7 did not result in a notable increase in metal levels. The two muscle samples taken from the same pike (pike sample #6 and #7) had metal levels which fell within the range of levels encountered in other fish in this study. The Ontario Ministry of the Environment has conducted an extensive fish sampling program for many years to accumulate the base-line information for an Ontario sport fish consumer guide (Ontario Ministry of the Environment, 1990). In this sampling program, metal knives have been used extensively to collect tissue for metal and organic residue determination without evidence of contamination (pers. comm. A. Vaillancourt, Ontario Ministry of the Environment).

3.3.5 Relationship of Metal Levels Among Different Media

Considering that sampling frequency and analytical techniques

Table 3.17 Total Metal Concentration (mg/kg) in Fish Muscle Tissue from the Forestburg Reservoir, November 1989.

	Cu		Zn		Ni		Cr		V		Hg		As		Se	
	wet	dry	wet	dry	wet	dry	wet	dry	wet	dry	wet	dry	wet	dry	wet	dry
White Sucker																
#1 male 43.0 cm	0.6	2.6	3	13	<0.2	<0.9	0.10	0.4	0.02	0.09	0.246	1.06	<0.007	<0.03	(0.06)	0.3
#2 male 36.4 cm	0.4	1.9	4	19	<0.2	<1.0	0.15	0.7	0.03	0.14	0.169	0.81	<0.007	<0.03	(0.04)	(0.2)
#3 female 45.0 cm	0.4	2.0	4	20	<0.2	<1.0	0.11	0.5	0.02	0.10	0.167	0.83	<0.007	<0.03	(0.06)	0.3
#4 female 41.7 cm	0.5	2.2	4	18	<0.2	<0.9	0.10	0.4	0.02	0.09	0.112	0.50	<0.007	0.03	(0.02)	(0.1)
#5 male 34.7 cm	0.4	1.8	4	18	<0.2	<0.9	0.14	0.6	0.02	0.09	0.104	0.46	<0.031	0.14	0.08	0.4
Northern Pike																
#1 female 57.4 cm	0.2	0.9	4	18	<0.2	<0.9	0.12	0.5	0.02	0.09	0.219	1.00	<0.007	<0.03	(0.06)	0.3
#2 male 45.9 cm	0.2	0.9	5	22	<0.2	<0.9	0.11	0.5	0.03	0.13	0.232	1.03	<0.007	<0.03	0.09	0.4
#3 male 54.9 cm	0.2	0.9	5	23	<0.2	<0.9	0.12	0.6	0.03	0.14	0.341	1.57	<0.007	<0.03	0.08	0.4
#4 male 36.2 cm	0.3	1.4	4	19	<0.2	<0.9	0.10	0.5	0.03	0.14	0.144	0.67	0.013	0.06	0.08	0.4
#5 male 46.2 cm	0.3	1.3	4	17	<0.2	<0.9	0.10	0.4	0.02	0.09	0.225	0.97	0.023	0.10	0.07	0.3
#6 female 36.3 cm	0.2	0.9	5	23	<0.2	<0.9	0.11	0.5	0.02	0.09	0.106	0.50	0.019	0.09	0.08	0.4
#7 female 36.3 cm	0.2	0.9	6	28	<0.2	<0.9	0.11	0.5	0.02	0.09	0.103	0.48	0.010	0.05	<0.07	<0.3

() values in parenthesis indicate measurable concentrations below the method detection limit

differed among media sampled in the Battle River, only broad comparisons of metal levels can be made among the different media. Table 3.18 summarizes the metal data in terms of means and ranges and provides the basis for such comparisons.

In the Battle River, as in most other rivers of Alberta (e.g., Shaw et al. 1990, Shaw et al. 1991), metal concentrations in water were generally low and all metals, except As, frequently occurred at or below the detection limit. With the exception of Hg, metals generally occurred at measurable concentrations in all other media.

A comparison of metal levels in sediments and biota gives some insight into the flux of metals through food chains. In the Battle River, Hg levels in water, sediments, plants, and invertebrates were most often below the detection limit. In fish, however, Hg levels were always measurable and at least an order of magnitude higher than the highest concentration measured in invertebrates. Campbell et al. (1988) indicate that biomagnification of trace metals (increase in concentration at higher levels in the food chain) has only been demonstrated adequately for Hg, but that biominification (decrease of concentrations at higher levels in the food chain) appears to occur more frequently. In the Battle River, it is probable that the higher levels of Hg in fish tissue relative to other biological tissues reflect biomagnification, whereas the lower levels of all other metals in fish tissue reflect biominification. Nickel provides a particularly good illustration of possible biominification as concentrations decline consistently with increasing trophic level. However, fish data from the Battle River may not be entirely suitable for assessing metal transfer along the food

TABLE 3.18 Summary of Metal Levels Recorded in the Battle River in Different Media
(concentrations as mg/L for water, and mg/kg dry weight for other media, Hg as wet weight)

	As	Cr	Cu	Ni	Se	V	Zn	Hg[1]	Cd	Pb
Water (Total) $\bar{x}$	0.0026	0.004	0.003	0.006	<0.0001 [3]	0.005	0.005	<.0001	<.001-.004	<.002-.010[2]
(min-max)	0.0008-0.0074	<.001-0.024	<.001-0.010	<.001-0.018	<.0001-.0002	<.002-0.018	<.001-.0028	<.001-.0001	<.001-.004	<.002-.010
Sediments $\bar{x}$	7.3 *	2.10	31.20	6.40	0.177 *	4.70	21.80	<0.010 *	<0.1	5.60
(0.5N HCl) (min-max)	3.6-26	0.70-23.95	1.16-35.55	3.09-20.81	0.022-0.584	0.17-9.27	7.83-41.91	<0.020-0.020	<0.07-0.27	2.16-12.15
Susp. Sediments $\bar{x}$	8.57 *	6.39	17.36	13.95	0.455 *	8.52	43.67	0.017 *	0.30	9.93
(0.5N HCl) (min-max)	7.8-9.8	3.72-11.07	13.41-20.18	11.40-15.71	0.209-0.782	7.01-9.89	27.39-58.14	0.013-0.023	0.10-0.43	8.81-11.34
Macrophytes										
-Stems & Leaves $\bar{x}$	1.82	2.3	4.4	5.6	0.19	4.33	18.9	<0.010	NA	NA
(min-max)	0.94-3.54	0.8-4.5	1.8-7.6	1.8-9.6	0.09-0.32	0.1-9.9	8.3-38.0	<.010-0.058		
-Rhizomes (roots) $\bar{x}$	129.85	12.4	8.5	7.9	0.19	23.73	34.2	<0.010	NA	NA
(min-max)	7.74-243.19	4.5-30.2	3.9-15.0	3.5-16.5	0.07-0.53	11.96-43.05	18.0-59.6	<0.010		
Filamentous Algae $\bar{x}$	8.13	4.8	6.6	6.0	0.20	7.9	19.3	<0.010	NA	NA
(min-max)	1.09-25.29	3.8-8.6	2.8-9.7	2.3-9.2	0.09-0.24	4.2-18.8	11.1-42.7	<0.010		
Invertebrates										
-Spring $\bar{x}$	11.50	3.7	37.7	3.0	NA	4.6	182	<0.010	NA	NA
(min-max)	1.39-24.4	<0.1-23	4.1-97	<0.1-13	-	<0.1-8	14-460	<0.010-0.020		
-Fall $\bar{x}$	2.20	1.9	34.9	3.2	0.9	2.3	124	<0.010	NA	NA
(min-max)	0.5-6.1	<0.1-5.0	3.4-97	<1-11	0.1-4.0	<0.1-7.2	7-420	<0.010-0.020		
Fish dry w. $\bar{x}$	<0.02	<0.5	1.5	<0.9	0.3	0.10	20	0.181	NA	NA
(min-max)	<0.03-0.14	<0.5-0.7	0.9-2.6	<0.9-<1.0	0.1-0.4	0.09-0.14	13-28	0.103-0.341		

[1] Hg sediment and tissue levels expressed as mg/kg wet weight
[2] Pb, dissolved
[3] "< detection limit" indicates most or all measurements below detection level (detection limit applies to wet tissue samples).
* hot acid extraction

chain. Indeed, Moore and Ramamoorthy (1984) comment on the unsuitability of fish muscle tissue for metal monitoring as metals tend to accumulate more in other organs (such as the liver, brain or gonads). Metal levels for whole organisms may be more appropriate in food chain studies.

Battle River data also illustrate the differences in bioaccumulation of various metals in different tissues, or organisms. On average, macrophyte roots and filamentous algae concentrate more As and V than any other tissue whereas invertebrates concentrate more Zn.

3.3.6 Comparison of Metal Levels in the Battle River to Objectives, Guidelines and other Published Data

Maximum acceptable levels of heavy metals have been defined for surface waters in the Alberta Surface Water Quality Objectives (ASWQO - Alberta Environment 1977), the Canadian Water Quality Guidelines (CWQG - CCREM 1987), the Saskatchewan Surface Water Quality Objectives (SSWQO - Saskatchewan Environment and Public Safety 1988) and the Prairie Provinces Water Quality Objectives (PPWBO, 1990). Few guidelines have been proposed for sediments (e.g., Persaud and Wilkins 1976, U.S. EPA, 1977, Sullivan et al. 1985 and Hart et al. 1988). There are no guidelines for aquatic organisms except for Hg levels in fish tissue (Ontario Ministry of the Environment 1990).

Water quality objectives and guidelines listed in Table 3.19 and shown on Figure 3.2 to 3.5 are for total metals except the PPWBO for As which apply to the dissolved fraction. In the Battle River, all water samples collected as part of this study complied with all guidelines for As, Se, and Hg. Metal levels did not exceed the ASWQO or guidelines for

Table 3.19 Water Quality Guidelines or Objectives[1] for Heavy Metals

	ASWQO[5] mg/L	CWQG[6] Aquatic Life mg/L	CWQG[6] Irrigation mg/L	PPWBO[7] mg/L	SSWQO[8] Aquatic Life mg/L	SSWQO[8] Irrigation mg/L
As	0.01	0.05	0.1	0.05[3]	0.05	0.1
Cd	0.01	0.0013-0.0018[2]	0.1	0.001	0.001	0.01
Cr	0.05	0.02-0.002[4]	0.1	0.011	0.020	0.1
Cu	0.02	0.003-0.004[2]	0.2 (sensitive crops) 1.0 (tolerant crops)	0.004	0.01	0.2
Pb	0.05	0.004-0.007[2]	0.2	0.007	0.02	0.2
Hg	0.0001	0.001	-	0.0001	0.0001	-
Se	0.01	0.001	0.02 or 0.05 (intermittent)	0.001[3]	0.01	0.02
Zn	0.05	0.03	1.0 (soil pH<6.5) 5.0 (soil pH>6.5)	0.03	0.05	1.0
Ni	-	0.025-0.150[2]	0.2	0.1	0.1	0.2

1 Metals concentration as total for unfiltered water unless stated otherwise
2 Values depend on hardness Hwy 611: 120-180 mg/L^{-1}, lowest guideline value applies
Other sites: >180 mg/L^{-1}, highest guideline value applies
3 Metal concentration as dissolved
4 Lowest value protects aquatic life, highest value fish only
5 ASWQO - Alberta Surface Water Quality Objectives (Alberta Environment 1977)
6 CWQG - Canadian Water Quality Guidelines (CCREM 1987)
7 PPWBO - Prairie Provinces Water Quality Objectives (PPWB 1990)
8 SSWQO - Saskatchewan Surface Water Quality Objectives (Saskatchewan Environment and Public Safety 1988)

irrigation (i.e. ASWQO and SSWQO). However, guidelines for the protection of aquatic life and PPWBO were exceeded regularly at all sites for Cd and Cr. These objectives were also exceeded for Cu at the three lower sites during periods of high river discharge. Zinc and Ni only occasionally exceeded these guidelines at the lower sites and Pb exceeded them only once at Hwy 872.

Sediment guidelines presented in Table 3.20 apply to total concentrations. Technically, only Hg and As data from the Battle River can be compared to these guidelines (no guidelines for Se given). All other metal determinations in the Battle River were carried out for non-residual metals and comparisons with guidelines are not valid. Mercury levels in Battle River sediments were always well below any of the guidelines. However, As levels always exceeded the U.S. EPA guidelines, and occasionally exceeded the MOE guidelines. Even the more lenient guidelines for As proposed by Sullivan et al. (1985) and Hart et al. (1988) were exceeded in the Battle River near the Mouth.

Guidelines for the consumption of fish (Joint FAO/WHO Expert Committee on Food Additives 1972) specify that Hg levels in muscle tissue should not exceed 0.5 mg/kg wet weight for unlimited consumption. None of the pike or suckers collected in the Forestburg Reservoir had Hg levels which exceeded this concentration.

Table 3.21 was compiled to try to compensate for the absence of metal guidelines or objectives for other media by comparing data from the Battle River with those from other studies, especially those carried out in Western Canada.

Metal levels presented in Table 3.21 for riverine sediments were

Table 3.20 Sediment Water Quality Guidelines for Heavy Metals[1] (µg/g)

	Hart et al. 1988	MOE[2]	U.S. EPA Region V[3]	WDNR[4]
As	1.2	8	3	10
Cd	2.5	1	-	1
Cr	75	25	25	100
Cu	65	25	25	100
Pb	55	50	40	50
Hg	0.6	0.3	1	0.1
Ni	75	25	20	100
Zn	145	100	90	100

[1] Guidelines are for total concentrations
[2] Open water dredge spoil disposal guidelines (Persaud and Wilkins 1976)
[3] Guidelines for the pollutional classification of Great Lakes harbour sediments (U.S. EPA. 1977)
[4] Wisconsin Department of Natural Resources interim criteria and guidance criteria for in-water disposal of dredge material (Sullivan et al. 1985).

Note: MOE and WDNR are guidelines for open-water disposal of dredge spoil.

TABLE 3.21 Metal Data from the Battle River Multi Media Study Compared to Those Reported in Other Studies

RIVER (LAKE)	As Total	Cr	Cu	Ni	Pb	V	Zn	Hg Total	Cd	Se Total	Source
A. SEDIMENTS (metals in mg/kg dry weight, Hg - wet weight)											
Battle R.	3.2-26.0	0.53-23.95 6.6-55.5	1.16-35.5 2.36-44.89	3.09-22.41 6.8-36.1	2.16-12.15 <4-10	0.17-9.27 12.3-37.7	8.07-41.91 19.5-83.3	<0.002-0.020	<0.07-0.27 <0.7	0.013-0.548	This study. Non-residual = 0.5N HCl <180 µm fraction Aqua Regia, hot extraction
North Saskatchewan R.	4.2-8.7	6.03-13.6	12.3-25.2	16.1-38.6	8.01-37.9	-	46.1-89.2	0.025-0.105	0.3-1.4	0.09-0.37	Shaw et al. (in prep) Total Metals
Athabasca R.	-	-	<1.0-12.0	-	-	<8.0-11.0	6.0-37.0	-	-	-	Allan & Jackson 1978 non-residual; 0.5N HCl
Ottawa R. (1972)	-	2-114	1-144	0-70	6-314	-	16-485	0.09-2.70	0.15-2.40	-	Oliver and Agemian 1974 Non-residual: Aqua Regia, cold extraction, sieved <180 µm
Ottawa R. (1982)	1.7-96.4	0.7-13.0	0.9-47.0	1.1-20.0	1.6-78.0	-	12.0-300.0	<0.1-0.19	0.1-2.7	-	Merriman 1987 Non-residual: 0.5N HCl
Fraser R.	-	-	31.1-32.8	31.4-32.7	44.6-162.1	-	26.6-113.4	0.065-0.108	below det.	-	Chapman et al. 1980 dried, <63 µm, H_2O_2+HNO_3
B. SUSPENDED SEDIMENTS (metals in mg/kg dry weight, Hg - wet weight)											
Battle R.	7.8-9.8	3.72-11.07 36.2-48.9	13.41-20.18 21.89-32.28	11.40-15.71 30.7-37.5	9.65-11.34 <4	7.01-9.89 32.3-45.3	27.39-58.14 72.7-115.5	0.013-0.023	0.10-0.43 <0.7	0.209-0.782	0.5N HCl - This study Aqua Regia, hot
Bow R.	-	22-60	20-120	20-31	10-180	-	80-190	0.05-0.60	0.2-0.9	-	Blachford and Ongley (1984)
Oldman R.	-	21-42	16-64	19-42	9-48	-	82-580	0.03-0.50	0.2-0.6	-	Aqua Regia, hot

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TABLE 3.21 Continued

RIVER (LAKE)	As Total	Cr	Cu	Ni	Pb	V	Zn	Hg Total	Cd	Se Total	Source
C. AQUATIC INVERTEBRATES (total metal concentrations as mg/kg dry weight, Hg - wet weight)											
Battle R.											
Spring $\bar{x}$	11.50	3.7	37.7	3.0	-	4.3	182.0	<0.01	-	-	This study.
Fall $\bar{x}$	2.20	1.9	34.9	3.2	-	2.4	123.6	<0.01	-	0.9	
Range	0.5-13.2	<0.1-23.0	3.4-95.0	<0.1-13.0	-	<0.1-24	7.3-458	<0.01-0.20	-	0.1-4.0	
Fraser R.											
Tubificidae	-	-	9.5-15.7	1.8-2.7	5.0-15.1	-	65.1-83.5	0.11-0.43	-	-	Chapman et al (1980) (Corrected for gut content)
Athabasca R.											
Hemiptera	-	1.6-4.5	18.7-32.6	5.7-43	22-40	<10	129-193	0.09-0.15	0.7-5.7	-	Lutz and Hendzel (1976)
Lakes Near Yellowknife											
Pelecypoda	1.0-3.6[A]										
Gastropoda	4.5-44.0[A] 100-250[B]										
Oligochaeta	820[B]										
Chironomidae	0.9-53[A] 29.0-380[B]										Wageman et al. (1978)
Hirudinea	1.8-26.0[A] 190[B]										[A] uncontaminated [B] contaminated
Amphipoda	5.1-31[A]										
Lakes & Rivers in Ontario											
Tubificidae											Persaud, Lomas and Hayton (1987)
mostly $\bar{x}$	5.3	-	36.1	-	9.5	-	216.3	0.3	0.3		contaminated and uncontaminated
range	0.7-21.6		9.6-82.0		0.1-60.6		62.9-663.4	0.1-0.5	0.1-1.2	-	waters (corrected for gut content
Environmental Range											
Unpolluted	<0.5-20	≤5	≤5	-	-	0.1-5	-	-	-	0.3-2.7	Moore and Ramamoorthy (1984) and
Polluted	-	-	5.0-200	0.1-45	39	-	3500	375	0.2-0.9	-	Moore (1990) values reflect range or highest value cited

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TABLE 3.21 Continued

RIVER (LAKE)	As Total	Cr	Cu	Ni	Pb	V	Zn	Hg Total	Cd	Se Total	Source
D. AQUATIC PLANTS (total metal concentration as mg/kg dry weight, Hg - wet weight)											
Battle R.											
Potamogeton stems & leaves	0.94-3.54	0.5-4.5	1.8-7.6	1.8-9.6	-	0.11-9.90	8.3-38.0	<0.010-0.058	-	0.09-0.32	This study range.
Potamogeton roots	7.74-243.19	4.5-30.2	3.9-15.0	3.5-16.5	-	11.96-43.05	18.0-59.6	<0.1	-	0.07-0.53	
Filamentous green algae	1.34-25.29	2.6-8.6	2.8-9.7	2.3-9.2	-	4.18-11.22	11.1-42.7	<0.1	-	0.09-0.24	
Bow R.											
Potamogeton whole	-	4-14	3-15	4-14	4-16	-	5-125	0.15-0.45	0.2-1.6	-	Blachford and Ongley (1984); values taken from graph, indicate range
Oldman R.											
Potamogeton whole	-	4-12	4-13	4-18	4-2	-	10-55	0.02-0.37	0.2-0.6	-	
Filamentous algae	-	10-21	9-15	9-17	6-8	-	26-42	0.04-0.22	0.2-0.3	-	
Lakes Near Yellowknife											Wageman et al. (1978) [A] uncontaminated lakes [B] contaminated lakes
Potamogeton	7.9[A]-920[B]	-	-	-	-	-	-	-	-	-	
Environmental Range											Moore & Ramamoorthy (1984) and Moore (1990) values reflect range or highest value cited
Unpolluted	<50	<5	-	-	-	-	<50	-	-	0.9-2.7	
Polluted	-	-	10-100	690	-	-	100-500	0.43	-	-	

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TABLE 3.21 Continued

RIVER (LAKE)	As Total	Cr	Cu	Ni	Pb	V	Zn	Hg Total	Cd	Se Total	Source
E. FISH (total metal concentrations as mg/kg wet weight)											
Battle R.											
White Sucker	<0.02-0.03	<0.1-0.2	0.4-0.6	<0.1	-	<0.1	3.2-4.4	0.10-0.25	-	0.02-0.08	This study, axial muscle
Northern Pike	<0.02-0.02	<0.1	0.2-0.3	<0.1	-	<0.1	4.1-5.9	0.10-0.34	-	0.02-0.09	
Athabasca R.											
Northern Pike	<0.01-0.04	-	0.48-0.84	-	-	-	27.5-47.7	0.05-0.33	-	0.15-0.42	Lutz and Henzel (1976)
White Sucker	0.02-0.07	-	1.13-2.2	-	-	-	9.4-12.1	0.06-0.17	-	0.19-0.44	whole fish
North Saskatchewan R.											
Northern Pike	-	-	-	-	-	-	-	0.31	-	-	AEC (1983) Average of mixed tissue sample
Waterton N.P.											
-Goat L.											
Cutthroat Trout	-	0.503	-	-	-	-	6.73	0.053	<0.05	0.90	Lockhart et al. (1990)
-Lone L.											muscle tissue, average for
Brook Trout	-	0.358	-	-	-	-	8.10	0.090	<0.05	0.608	several fish; collections in
Cutthroat Trout	-	0.377	-	-	-	-	6.30	0.051	<0.05	0.243	July and August
-Lineham L.											
Cutthroat Trout	-	0.407	-	-	-	-	10.60	0.039	<0.05	0.487	
-Twin L.											
Cutthroat Trout	-	0.430	-	-	-	-	8.88	0.069	<0.05	0.225	
Brook Trout	-	0.318	-	-	-	-	7.60	0.068	<0.05	0.683	
Environmental Range											
Unpolluted	<0.1-0.4	<0.25	-	-	-	-	0.5-33	-	-	0.4-9.8	Moore & Ramamoorthy (1984) and
Polluted	-	-	-	0.18	0.65	0.02	-	1.35	-	-	Moore (1990) values reflect range or highest value cited

obtained by different sampling and analytical methods and only general comparisons can be made. Arsenic, Se, Cu, and Cr levels appear to be higher in the Battle River than in the North Saskatchewan River, but levels of Ni, Pb, Zn, Hg, and Cd are higher in the North Saskatchewan River.

Vanadium and Zn levels given by Allan and Jackson (1978) for the Athabasca River are similar to those in the Battle River, but Cu levels are somewhat higher in the Battle. Contrasting with metal sediment data from Alberta Rivers are the much higher metal levels reported for a contaminated portion of the Ottawa River (Ontario) by Oliver and Agemian (1974) and by Merriman (1987). Except for Cu levels, metal levels in the lower Fraser River (B.C.) are also higher than those found in the Battle River.

A comparison of results of hot Aqua Regia extraction of suspended sediments from the Bow and Oldman rivers (Blatchford and Ongley 1984) with those from the Battle River indicates that metal levels were generally higher in suspended sediments from the two southern rivers.

Some root samples of Potamogeton richardsonii had levels of As, Cr, and Zn which slightly exceeded the range given by Moore and Ramamoorthy (1984) for uncontaminated waters. However, metal concentrations in stems and leaves of P. richardsonii and in filamentous green algae of the Battle River were lower than those reported by Blatchford and Ongley (1984) for the Bow and Oldman rivers. Although the inclusion of roots in that study may explain the higher concentrations found there for the macrophyte, differences in metal levels in filamentous green algae in that study and this one are probably real.

Although the levels of Hg, Zn, Ni, and As in Battle River invertebrates were well below the range for contaminated areas, the highest Cu concentrations in the Battle River have reached the lower end of this range (Moore and Ramamoorthy 1984). Arsenic levels in invertebrates from the Battle River correspond to levels recorded in uncontaminated lakes near Yellowknife and were much lower than those of contaminated lakes (Wageman et al. 1978). Maximum concentrations of Cu, V, and Zn recorded in invertebrates from the Battle River were higher than the maxima for invertebrates in the Athabasca River (Lutz and Henzel 1977), but the latter had higher Cr and Hg levels. Compared to invertebrates in lakes and rivers in Ontario (Persaud et al. 1987), Battle River invertebrates tended to have similar levels of Cu and Zn, but somewhat lower levels of As and Hg.

Arsenic, Cr, and Zn levels in fish from the Battle River were typical of unpolluted waters (Moore and Ramamoorthy 1984). Mercury levels in fish from the Battle River were higher than those in fish from Waterton Lakes (Lockhart et al. 1990), but similar to those from the Athabasca River (Lutz and Henzel 1977) and the North Saskatchewan River (Alberta Environmental Centre 1983). Selenium levels were somewhat lower in fish from the Battle River than from Waterton Lakes.

3.4 SUMMARY AND CONCLUSIONS

The Battle River Multi-Media Monitoring project was undertaken to assess the suitability of water, bottom sediment, suspended sediment and biota for monitoring heavy metals in the Battle River. The development or improvement of sampling and analytical methods and the

evaluation of seasonal and longitudinal trends were important components of this study.

Battle River biota, sediments and water were sampled at seven key locations (i.e. Hwy 611, Hwy 53, downstream Camrose Creek, Forestburg Reservoir, Hwy 872, Unwin and near the Mouth) and on one (plants, suspended sediments and fish), two (invertebrates) or six (sediments and water) occasions to determine spatial and temporal changes in concentrations of contaminants.

3.4.1 Method Selection and Development

3.4.1.1 Sampling Methods

Standard protocols, equipment tested elsewhere, or straightforward collection techniques were suitable for the sampling of water (grab samples), sediments (Ekman dredges), suspended sediments (Sedisamp system), fish (gill nets), and plants (visual search and collection). Sampling required seconds (water) to hours (suspended sediments) and one or two people. In contrast, the sampling of benthic invertebrates was time consuming, labor intensive and required a crew of several people. The low sampling efficiency is due to the need to collect large numbers of specimens to meet analytical requirements, and to intrinsic characteristics of most riverine zoobenthos (e.g., small specimens which are tedious to extract from the sediments, detritus and vegetation with which they are intimately associated).

3.4.1.2 Analytical Methods

Analytical methods for metal determination for sediment and

biological samples were selected and implemented at Alberta Environmental Centre by the Water Analysis and Research Branch (see Section 2).

Two extraction methods (hot Aqua Regia and cold 0.5N HCl) were used to extract non-residual metals (Cu, Cr, Cd, Zn, Ni, Pb, and V) from sediments. A comparison of the two data sets suggests that either method could be used to determine temporal and spatial trends in sediment metal levels. Although the hot extraction had a higher recovery rate for most metals, the milder cold extraction in 0.5N HCl had an excellent precision, was less labour intensive and more suitable for the determination of Cd and Pb.

Total metals were determined on all biota samples. The levels measured in aquatic invertebrates may over-estimate actual tissue concentrations since some trace metals entrained in the silica matrix of sediments ingested with food particles may be extracted. For valid comparisons of metal concentrations among media, concentrations must be expressed as weight per unit dry weight.

3.4.2 Spatial and Temporal Trends in the Battle River

An appraisal of spatial and temporal trends in concentrations in any medium requires a good understanding of environmental factors which influence metal levels in that medium. If natural variability is large, changes in concentration due to anthropogenic influences will be more difficult to measure.

3.4.2.1 Water

Total metal concentrations in <u>water</u> were highly correlated with

river discharge and NFR levels. Consequently, it was difficult to dissociate the increase in total metal concentrations in water which occurs in downstream direction or during spring run-off from the increase in river discharge and NFR levels. Dissolved metal concentrations were independent of discharge and while seasonal trends were not readily apparent, there were longitudinal increases in median concentrations in a downstream direction.

3.4.2.2 Sediments

Metal levels in sediments were highly correlated with levels in the organic content of the sediments, and longitudinal and seasonal changes in sediment metal levels can be largely explained by differences in sediment characteristics. Levels of Pb in Battle River sediments were not entirely related to sediment characteristics and may be influenced by anthropogenic activities (burning of leaded gasoline and coal). The gradual increase in Cu and Zn among the three upper sites may also originate from anthropogenic sources.

3.4.2.3 Suspended Sediments

Despite the limited size of the suspended sediment data base (i.e. three samples), it is apparent that organic matter and particle size influence metal concentrations in a way similar to depositional sediments. Longitudinal trends in suspended sediments correspond to trends in bottom sediments but, because the organic content of suspended sediments was higher and particles were finer, metal levels tended to be higher in suspended sediments.

3.4.2.4 Biota

The interpretation of metal levels in biological tissue can be considerably more complex than in sediments or water. Dynamic physiological processes have as much or more influence on the ultimate metal levels or body burdens measured in organisms as the ambient metal levels (i.e. metals in water, sediments, or food). In an attempt to control some of the variability related to physiological differences, an effort was made to collect samples which were uniform in terms of specimen size and taxonomy, or which consisted of one type of tissue.

3.4.2.4.1 Plants

Plant data confirmed that metal concentrations varied appreciably among plant species, but also among plant parts. Metal levels were generally high in roots of P. richardsonii, low in the stems and leaves of this macrophyte and intermediate in filamentous green algae. Longitudinal patterns were best defined in stems and leaves and corresponded well to longitudinal patterns in water. The potential value of these plant parts as time integrators of trace metal concentrations in water should be explored further. The increase of As in downstream direction was considerably more notable in macrophyte roots than in any other medium.

3.4.2.4.2 Invertebrates

Metal concentrations differed considerably among invertebrate taxa. Simuliidae contained the highest concentration of As, Cr, Ni, and V; Amphipoda and Gastropoda had the highest Cu concentration;

and Zn levels were highest in Hirudinea. Inclusion of shells in the tiny Sphaeriidae clams likely contributed to lower levels of As, Cu, Cr and Zn than in large clams (Unionidae) which were analysed without shells. Seasonal differences, likely related to changes in life stage and metabolic activity, were reflected in lower levels of As, Cr, Zn and V and less frequent detections of Hg in fall samples compared to spring samples. Variability among duplicate samples was low if samples consisted of large numbers of specimens (e.g., Amphipoda, Gastropoda), but variability was large and inconsistent for different metals among single unionid clams. With the possible exception of Hg and Ni there was no evidence of longitudinal trends in benthic invertebrate body burdens.

3.4.2.4.3 Fish

Metal levels in muscle tissue from the two fish species sampled in the Forestburg Reservoir showed low intra-specific and inter-specific variability. Only Cu levels differed significantly between the two species. Fish muscle was the only medium in which Hg was detected consistently.

Levels of Hg in fish tissue reflect biomagnification along the food chain. There was no evidence of biomagnification of other metals, instead, the lower levels of metals measured in fish muscle compared to invertebrate tissue or plants suggest biominification.

3.4.2.4.4 Comparison of Battle River Data with Published Information

Metal concentrations in water sediment and biota were compared to guidelines or objectives whenever possible, and to comparable

results from other studies in Western Canada.

- CWQG for the protection of aquatic life and PPWB objectives were exceeded regularly at all sites for Cd and Cr concentrations in water. These objectives were also exceeded at the three lower sites during periods of high discharge for Cu, and occasionally for Zn and Ni; Pb exceeded these objectives once at Hwy 872.

- Guidelines for sediments apply to total metals and valid comparisons were restricted to Hg, and As. Hg levels in the Battle River sediments were lower than any of the guideline values, but As often exceeded the guidelines.

- Hg guidelines for the consumption of fish (Joint FAO/WHO Expert Committee on Food Additives 1972) are the only guidelines for aquatic biota; they were met by all fish samples analysed in this study.

- Metal concentrations in Battle River sediments were generally much lower than in rivers such as the Ottawa (Ontario) or the Fraser (British Columbia) which flow through heavily industrialized or more densely populated areas. However, levels of As, Se, and Cr were higher than in the North Saskatchewan River and Cu levels were higher than in the Athabasca River.

- Suspended sediments and plants from the Battle River tended to have lower concentrations of metals than those from the Bow and Oldman rivers.

- Levels of Hg, Zn, Ni, and As in invertebrates were typical of levels encountered in uncontaminated areas of the world, although Cu levels were at the upper end of the range. Levels of Cu, V and Zn were somewhat higher in invertebrates from the Battle River than from the Athabasca River. Levels of As, Cr, and Zn in fish were typical of unpolluted waters.

On the basis of these comparisons, it is likely that metal levels in the Battle River reflect natural levels, even though some (As and Cu) are rather high.

3.4.3 Advantages and Disadvantages in the Routine Monitoring of Certain Media

Advantages and disadvantages involved in the collection of metal data from various media for the purpose of monitoring ambient levels in aquatic systems are listed below. It is important to note that this list would likely be different if the purpose of data collection was for more specialized studies such as transfer of metals along the food chain, or partitioning of metals among various media. Factors which were considered here are: sampling (e.g., ease of collecting representative samples, equipment and expertise required), sample processing (e.g., availability of protocols), data (e.g., degree and cause of natural variability, comparability of data with other data or quality standards).

MONITORING ADVANTAGES	MONITORING DISADVANTAGES
WATER	
• easy to sample • well-established analytical protocols • large pool of comparable data • guidelines for protection of various users are available	• concentration of total metals influenced by river discharge and suspended sediment concentration • concentration of total metals may in some cases not reflect anthropogenic inputs, or importance to aquatic life • high frequency of below detection values
SETTLED SEDIMENTS	
• easy to sample in small river with low or steady discharge	• more difficult to sample in large river with fluctuating discharge • total metals reflect residual and non-residual metal concentrations, and may not reflect anthropogenic inputs or importance to aquatic life • no consensus regarding best method to measure non-residual metals
• rather large pool of data, but... • little or no seasonality in Battle River suggests that a small number of samples is sufficient to describe baseline data • concentrations usually above analytical detection	• heterogenous data base often makes direct comparisons of data sets invalid • concentrations strongly influenced by sediment characteristics (e.g., particle size, TOC) • few guidelines for protection of various users.

SUSPENDED SEDIMENTS

- measure of metals associated with particles and transported by water
- lower frequency of values below the analytical detection limit than in water
- expensive and complex sampling gear
- qualitative and quantitative dependence on discharge
- many disadvantages listed for settled sediments also apply to suspended sediments.

PLANTS

- easy to sample in large quantities
- macrophytes may be suitable time-integration of metal levels in water over the growing season
- immobile, reflect conditions at sampling site
- interferences with metal levels associated with Aufwuchs or sediments are possible especially in filamentons algae
- pronounced differences in metal concentrations among various plant parts
- potential difficulty in determining source of metal (water? sediments?)
- seasonality in metal levels likely to occur as result of seasonal changes in physiological activity
- use of aquatic plants restricted to growing season and by their distribution.

INVERTEBRATES

- Ubiquitous component of aquatic food chains
- relatively immobile organisms, reflect conditions at sampling location
- life-span extends over longer period than vegetative growing season, greater potential than plants to integrate contaminant levels over longer time span
- sampling is labour intensive, and locally disruptive to ecosystem. Clean, large samples are difficult to obtain
- large degree of variability in the data, apparently related to seasonal changes in physiological activity, and intra- and inter-specific differences
- difficulty in differentiating metals associated with ingested sediments or absorbed to body wall from assimilated metals.

FISH MUSCLE

- fish are at or near top of aquatic food chains, easiest medium to detect biomaginification. Probably best medium to monitor mercury
- excellent replication among muscle tissue samples from various fish; few samples required.
- fish are very mobile, origin of contaminants may be difficult to determine
- fish are able to regulate metal levels in muscle tissue. Data may be unrelated to ambient changes.

3.5 RECOMMENDATIONS

1. There is a definite value in obtaining comparable measures of trace metal levels across the media selected for monitoring. Total metals and non-residual metals are recommended for routine monitoring. "Totals" reflect overall concentrations present, whereas "non-residual" reflect anthropogenically derived metals and also provide a measure for biologically available metals. Total metals have been measured more commonly and consequently results can be compared to a broader data base while methods for the determination of non-residual metals have been developed for sediments, only. Although total and non-residual metal levels are adequate in the routine monitoring of surface waters, it is evident that metal speciation is considerably more informative in the monitoring of toxic effluents.

2. In the monitoring of settled or suspended metal levels it is essential to document physical and chemical characteristics of the sediments such as particle size distribution, organic carbon, moisture, calcium carbonate, manganese and iron content, since all of their characteristics influence metal concentrations (e.g., Campbell et al. 1988). Seasonality does not appear to be an important consideration in the monitoring of sediment metal levels in streams with hydrogeological features similar to those of the Battle River.

Minimum sampling frequency for suspended sediment should include a sampling at high flow to reflect transport within the basin and at low flow to reflect the effect of point sources (see Ongley 1987). The timing of settled sediment sampling was not important in the Battle River where seasonal fluctuations in discharge are small. In rivers where

discharge changes are more important, sampling after a period of low and declining flows would be preferable.

Since metal levels in suspended and settled sediments are a function of sediment characteristics and, for suspended sediments of river discharge, it would appear reasonable to normalize these environmental variables in order to enhance the spatial and temporal comparability of sediment data. In doing this the value of instream sediment monitoring in the assessment of anthropogenic contamination would also be enhanced. Effective normalization procedures should rely on mathematical expressions of metal levels as a function of environmental variables which should be derived from a much larger data set than was available for the Battle River.

3. Except for fish tissue, there is not enough baseline information (from the Battle River, or in the general literature) to appreciate the full value of body burden data in routine monitoring of metals in freshwater aquatic environment. Baseline data describing seasonal and spatial variability in metal levels are needed; more information is required on the ability of aquatic organisms to regulate, or control the accumulation of metals in their tissues.

Based on data from the Battle River, it is recommended that special care be taken to standardize the sampling of biota which are to be analysed for trace metals. Samples should be collected at the same time of year and should consist of many specimens from the same taxonomic group and of similar size.

Macrophyte data from the Battle River showed the most consistent and best defined longitudinal patterns and it is recommended that the

potential value of these organisms as time integrators of trace metal concentrations in water be investigated further.

Based on Battle River data and literature data, fish muscle is recommended for the monitoring of Hg, a metal which biomagnifies along the foodchain.

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4. MULTI-MEDIA STUDY OF PESTICIDES IN THE BATTLE RIVER

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4.1 INTRODUCTION

In the past, pesticide monitoring programs in Western Canada have tended to concentrate on water, with analyses of other aquatic media restricted to short duration surveys or special studies. Reasons for this focus on water have included the ready availability of extraction and analytical methods for water samples, less-complex sampling protocols, and greater interpretability of water results (in the short term) due to the availability of guidelines, objectives, and comparable environmental data bases.

The information provided by most water-only monitoring programs has been limited, perhaps not justifying the significant analytical costs to achieve it. The data bases tend to be laden with 'less thans' which, while providing the information necessary to verify compliance with guidelines for water, are of limited value in determining concentration baselines and long term trends. The sparsity of data on pesticide residues in sediment and biological tissues has made it difficult to answer many fundamental questions regarding the quality of aquatic ecosystems. Incomplete answers remain as to the environmental fate of pesticide residues, the relationships between concentrations in various media, the mechanisms of inter-media transport, and potential biological effects. Attempts to answer these questions have to date depended largely upon laboratory experimentation, supplemented by limited environmental databases on specific residues.

In recent years, analytical techniques for pesticide residues in sediment and biological tissue have become more widely available. As well, large sample water extractors (LSEs) have been developed which effectively lower analytical

detection limits in water by an order of magnitude or more below those available for one litre samples. A purpose of this study was to examine a variety of media and methods in the Battle River Basin to determine their applicability for future monitoring programs.

Specific objectives of this study were to:

1. Investigate and select methods for sampling and analyses of pesticides in a variety of media;
2. Assess the value of various media in the routine monitoring of these contaminants;
3. Evaluate the data from longitudinal and seasonal surveys and assess their potential value in long-term monitoring programs;
4. Recommend multi-media monitoring methods.

4.1.1 Potential Sources of Pesticides in the Battle River Basin

A large number of agricultural, industrial, and domestic pesticides have been used in Canada over the past four or five decades. The top-selling agricultural herbicides in Alberta during the 1980's included triallate, MCPA, 2,4-D, trifluralin, diclofop-methyl, and bromoxynil (Constable 1990). These compounds fall into one of two analytical groups. The acidic herbicides are a closely related group of organic acid/ester derivatives having similar chemical properties. The neutral herbicides are a more diverse group of compounds from several chemical families having variable properties.

Annual Alberta usage of the popular herbicides ranges from a few hundred to over one thousand metric tonnes (Constable and Bharadia 1990). Sales figures for the

Battle River are not available. However, based upon the mixed agricultural nature of the basin, Battle River usage patterns likely reflect Alberta usage proportionally.

Lindane and methoxychlor are the only organochlorine insecticides currently used agriculturally in Canada. The remainder are under control for specific restricted uses, or have been de-registered from Canadian use. Use of organochlorine pesticides remains significant, however, in many less-developed countries. The organochlorines have attracted significant scientific interest in the past decades due to their persistence, toxicity, and tendency to bioaccumulate. As well, the evidence suggests that long range atmospheric transport of many of these compounds occurs (Gregor and Gummer 1989, CCREM 1987).

While agricultural application is the major potential source of pesticide contamination in the Battle River Basin, other potential sources include: industrial use for vegetation control near roadways, powerlines, oil and gas facilities, and other structures; domestic sources; accidental spills; careless cleaning and disposal of pesticide containers; landfill seepage; and mobilization of persistent archived residues sorbed to sediment.

Pesticide residues can enter surface waters by a number of pathways. These include direct overspraying of waterways, drifting vapours during spraying, surface runoff from fields during spring melt or rainfall events, long range transport in rain or snow, biological translocation, and groundwater recharge from treated areas. Nicholaichuk and Grover (1983) reported that for most pesticides, movement from fields to watercourses is less than 0.5% of amounts

applied, unless significant runoff occurs within one or two weeks of application.

The mobility and environmental fate of pesticide residues depend factors such as: the chemical and physical properties of the pesticide; the application rate,timing and method; soil characteristics; land features and hydrology; climatic conditions; levels of biological uptake and metabolism, and; rates of volatilization, phototodegradation, and chemical degradation. Complex interrelationships between these factors determine whether or not residues are likely to enter aquatic systems, how they will partition between aquatic compartments, and the degree to which they will persist and/or accumulate.

4.2 METHODS

4.2.1 Study Design

4.2.1.1 Sampling Locations

Multi-media sampling stations were established at six locations along the Battle River (Table 4.1, Figure 1.1). Sites were chosen to provide good longitudinal coverage of the basin from headwaters to mouth, while allowing ease of access. Brief station selection rationales are outlined following Table 4.1.

Table 4.1 Multi-Media Sampling Sites in the Battle River Basin 1989-1990

Site	NAQUADAT Code	Distance from Source (km)
Highway 611	00AL05FA0250	49
Highway 53	00AL05FA0280	89
Downstream of Camrose Creek	00AL05FA0750	273
Highway 872	00AL05FC1000	518
Unwin	00SA05FE1000	826
Near Mouth	00SA05EF1000	1030

Highway 611: located near the headwaters and least affected by human activity. Substantial oil and gas exploration and extraction in this area.

Highway 53: upstream of Wolf Creek, this parkland location is influenced by agricultural activities in the upper portion of the basin.

D/S Camrose Creek: affected by the discharges from the four largest municipalities in the upper portion of the basin (Lacombe, Ponoka, Wetaskiwin, Camrose). Drains an area of prime agricultural land.

Highway 872: located downstream of an area with active surface coal mining and a coal-fired generating plant.

Unwin: influenced by agricultural activities and oil and gas development. Long-term PPWB monitoring location.

Near Mouth: located just above the Battlefords, reflects agricultural activities in the Saskatchewan portion of the basin and cumulative impacts of activities throughout the basin.

4.2.1.2 Sampling Schedule, Media, and Analytical List

Longitudinal surveys of water and bottom sediments were conducted on six occasions. The surveys were scheduled to allow interpretation of seasonal variability. Other aquatic media were sampled less frequently (Table 4.2).

Table 4.2 Battle River Study Sampling Schedule

Medium	1989 May	June	August	Sept	Nov	1990 Jan	April
Water (Unfiltered)	X	X	X	X		X	X
Bottom Sediment	X	X	X	X		X	X
Suspended Sediment							X
Aquatic Invertebrates		X		X			
Macrophytes/Algae			X				
Fish Tissue					X		X

Large volume unfiltered water samples (20 to 40 litres) were collected at all stations during the first five longitudinal surveys. Samples were extracted in the field, using a Goulden Large Sample Extractor (GLSE). During April 1990, 20-litre unfiltered samples from three stations were extracted using a Pressure Container Sample Extractor (PCSE). Unfiltered One litre grab water samples were collected monthly from the PPWB monitoring location at Unwin, which was also a multi-media study sampling site.

Each survey, bottom sediment samples were taken at all multi-media sites. Bottom sediments were top 1 cm. composites from at least ten Ekman dredges. Suspended sediments from Hwy 611, d/s Camrose, and Unwin were collected with an Alfa-Laval Sedisamp System centrifuge (Envirodata 1981) during a major rainfall event in April, 1990.

Aquatic invertebrates were collected opportunistically at the six multi-media sites during June 1989 and late September 1989. Of 40 taxon-specific samples collected, 33 were analyzed for pesticide residues. Two taxa of aquatic plants (filamentous algae, Potamogeton richardsonii) were collected in August 1989 from Hwy 611, d/s Camrose, and Unwin.

Composite muscle and liver from northern pike and white suckers were analyzed from an initial fish survey in November, 1989. The November results prompted an additional fish collection in April 1990, at which time livers only were taken for analyses. Fish were collected from Forestburg Reservoir, located in the west-central portion of the basin. A brief summary of the samples analyzed for pesticide residues is provided in Table 4.3.

Table 4.3 Summary of Aquatic Media Analyzed

Medium	Sampling Method	# of Analyses
WATER	unfiltered 20-40 litres six multi-media stations field extracts (GLSE)	30
	unfiltered 20-litres three multi-media stations field extracts (PCSE)	3
	unfiltered 1.1 litre Unwin station only lab extracts (grab samples)	11
SEDIMENT	bottom sediment (top 1.0 cm) Ekmann dredge composites	30
	suspended sediment Alfa-Laval Sedisamp	3
BIOTA	aquatic invertebrates (8 taxa) six multi-media stations	33
	aquatic plants three multi-media stations filamentous algae and Potamogeton richardsonii	6
	fish (muscle and liver) Forestburg Reservoir northern pike, white sucker	10
	Total:	126

Thirty-eight pesticide residues (Table 4.4) were analyzed, including 11 acidic herbicides, 8 neutral herbicides, and 19 organochlorine insecticides. Results for the non-pesticide polychlorinated biphenyls (total congeners), which are usually co-analyzed with the organochlorine insecticides, are reported as well. Neutral herbicides and organochlorine/PCBs were analyzed in all media; acidic herbicides were analyzed in water samples only.

This multi-residue analytical list (Table 4.4) has been used for several years by a number of provincial and federal agencies. It reflects both levels of Canadian usage and environmental-regulatory concern. Eight of the ten most popular agricultural herbicides in Alberta (1981-1987) are included (Constable 1990). High use herbicides not analyzed include glyphosate (Roundup) and difenzoquat (Avenge), both of which are relatively immobile after application, binding strongly to soils (CCREM 1987, pers. comm. W. Inkpen, Alberta Environment). Analytical methods for glyphosate are not currently available at most laboratories.

Table 4.4 Battle River Study Pesticide Analytical List

Compound	Group	Analytical Detection Limits		
		Water 1.1 L ng/L	Water LVE ng/L	Sediment/Biota (dry) (wet) ng/G(ppB)*
MCPA	Phenoxy Acid Der.	30.	0.3	NA
2,4-DP	Phenoxy Acid Der.	30.	0.3	NA
2,3,6-TBA	Phenoxy Acid Der.	30.	0.4	NA
2,4-D	Phenoxy Acid Der.	30.	0.4	NA
Bromoxynil	Phenol Derivative	30.	0.3	NA
Silvex	Phenoxy Acid Der.	30.	0.3	NA
2,4,5-T	Phenoxy Acid Der.	50.	0.4	NA
MCPB	Phenoxy Acid Der.	50.	0.4	NA
2,4-DB	Phenoxy Acid Der.	50.	0.4	NA
Picloram	Piclonic Acid Der.	50.	0.5	NA
Dicamba	Benzoic Acid Der.	30.	0.3	NA
Trifluralin	Dinitroanaline	5.	0.4	0.2, 1.0
Diallate	Carbamate	100.	6.5	4.0, 4.0
Triallate	Carbamate	10.	0.7	0.2, 2.0
Atrazine	Triaz. and Acet.	50.	3.0	15., 4.0
Barban	Carbamate	100.	7.6	4.0, 4.0
Diclofop-Methyl	Miscellaneous	50.	3.4	1.5, 4.0
Endaven	Neutral Herb.	25.	2.1	1.0, 2.0
Metolachlor	Triaz. and Acet.	NA	NA	25., 4.0
Hexachlorobenzene	Organochlorine	1.	0.07	0.2, 4.0
a-BHC	Organochlorine	1.	1.3	0.4, 4.0
g-BHC	Organochlorine	1.	0.4	0.4, 4.0
Heptachlor	Organochlorine	1.	0.11	0.4, 4.0
Aldrin	Organochlorine	1.	0.07	0.6, 4.0
Hept Epoxide	Organochlorine	2.	0.06	0.1, 4.0
g Chlordane	Organochlorine	2.	0.04	0.2, 4.0
a Chlordane	Organochlorine	3.	0.07	0.2, 4.0
a Endosulphan	Organochlorine	1.	0.05	0.15, 4.0
b Endosulphan	Organochlorine	3.	0.09	0.65, 4.0
Endrin	Organochlorine	2.	0.14	0.25, 4.0
Dieldrin	Organochlorine	2.	0.18	0.2, 4.0
pp-DDE	Organochlorine	1.	0.2	0.5, 4.0
op-DDT	Organochlorine	1.	0.26	0.65, 4.0
pp-TDE	Organochlorine	2.	0.22	1.0, 4.0
pp-DDT	Organochlorine	4.	0.28	1.25, 4.0
Mirex	Organochlorine	1.	0.11	0.3, 4.0
pp-Methoxychlor	Organochlorine	10.	1.6	2.5, 4.0
Total PCB	Organochlorine	2.	3.3	25., 9.0

*Detection limits for sediments and biota changed in early 1990 following a laboratory re-evaluation of the analytical method. The two numbers listed are the detection limits for pre-1990 and for post-1990 respectively. Sediment results are based on dry weight; biological samples based on wet weight.

4.2.2 Field Methods

4.2.2.1 Goulden Large Sample Extractor (GLSE)

The GLSE is a liquid-liquid continuous flow extractor designed for pre-concentration (in dichloromethane) of hydrophobic trace organic contaminants from large-volume water samples. Among the benefits of large sample extraction are the minimization of analyte breakdown during shipping-storage, reduced shipping cost, and elimination of the need for sample preservation. In addition, large sample sizes (20-40 litres or greater) reduce analytical detection limits for most organic contaminants to what may be termed ultra-trace levels (less than 1 ng/L).

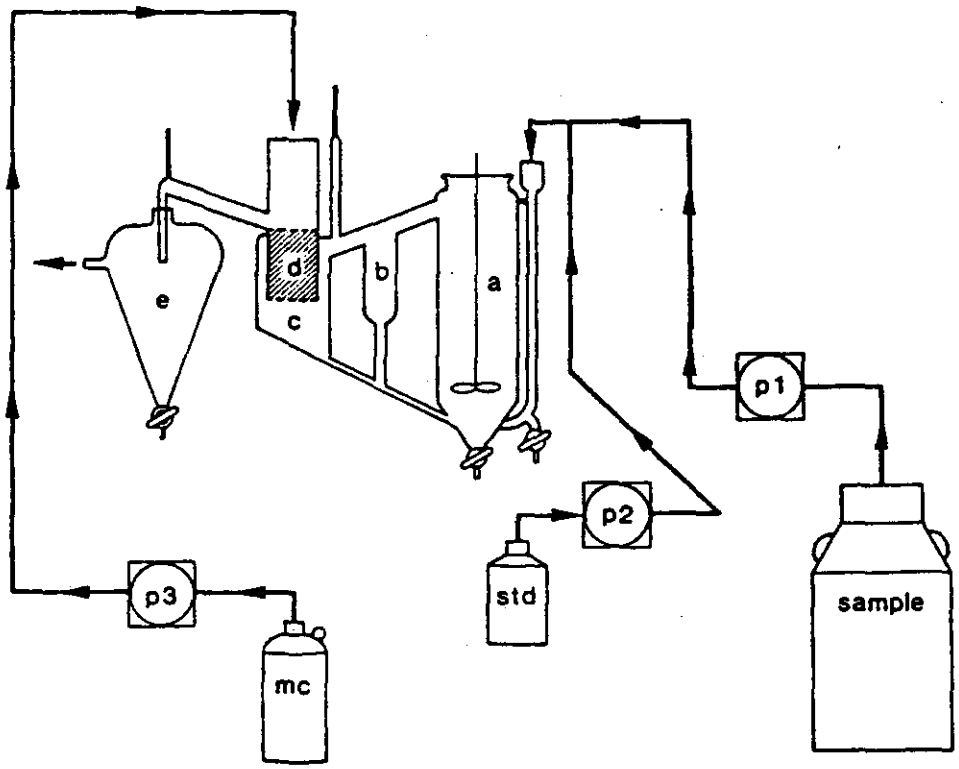
The GLSE was originally developed for projects in the Great Lakes-Niagara River region, where it has been used extensively for extraction of organochlorine/PCBs and other relatively non-polar residues from filtered or centrifuged samples. GLSE pre-concentration of herbicides and other analytes having lower hydrophobicity has, to date, been less common, and the method remains unvalidated for these classes of compounds (pers. comm. D. Anthony, Research Chemist, NWRI).

A schematic of the GLSE is presented in Figure 4.1. In-depth descriptions of the GLSE method and validation-testing results are available in Goulden and Anthony (1985), Anthony (1991), Neilson et al (1988), Neilson and Stevens (1988), Foster and Rogerson (1990), and Gregor and Gummer (1989).

The GLSE and all teflon tubing were cleaned between surveys using methods similar

to those used for cleaning pesticide sample bottles, with the oven-baking step omitted. The protocol included detergent washing, deionized water rinses, organic-free Milli-Q water rinses, and acetone-hexane-DCM rinses, followed by air drying (Water Quality Branch 1983). During surveys (between stations) the GLSE was rinsed with organic-free water until glassware was clean to the eye, rinsed with DCM to reduce carry-over between sites, and sealed for transport with baked aluminum foil.

Figure 4.1 Schematic of the Goulden Large Sample Extractor (from Foster and Rogerson 1990)



Schematic representation of the Goulden large-sample extractor: (a) mixing chamber, (b) first and (c) second stage settling chambers, (d) packed column, and (e) third stage settling chamber; fluid metering systems including (p1) sample, (p2) standard (std), and (p3) methylene chloride (mc) make-up pumps.

All sampling bottles and extract sample containers were washed according to pesticide protocols (Water Quality Branch 1983). Center-vertical depth-integrated water samples were collected in 4 x 4-litre glass bottles suspended in a weighted 4-litre bottle holder. All samples were extracted unfiltered and at ambient temperature. The time between sampling and extraction averaged 20 minutes, and did not exceed 40 minutes.

An initial volume of 150 mL dichloromethane (DCM, pesticide grade from Burdick and Jackson) was added to the GLSE mixing chamber prior to commencement of extraction. Sample water was passed through the GLSE in a single pass via a metering pump at a rate of 400 mL/minute. A high speed centrifugal pump was adjusted to provide efficient mixing of the water and solvent phases. A second metering pump replaced DCM lost due to solubility (DCM is approximately 1.6% w/w soluble in water) and volatilization. The DCM make-up rate was set at 10-12 mL/minute. Pumps and mixer were stopped occasionally to check the DCM level in the mixing chamber. The solvent trap made it possible to return to the mixing chamber any DCM able to escape over the teflon-chip column. This step was frequently necessary due to DCM emulsion.

Two extracts were required to accommodate the analytical list (Table 4.4). Samples were first extracted at ambient pH for neutral herbicides and organochlorine/PCBs. Surrogate organohalide recovery standards (1,3,5-tribromobenzene, 1,2,4,5-tetrabromobenzene, and delta-BHC in 100 mL methanol) were added via a third metering pump at a rate of approximately 1.5 mL/minute. After the surrogate container was empty, in about 70 minutes, additional methanol was flushed through at a rate of 5 mL/minute to purge the tubing. Sample volumes

of 40 litres were extracted on all occasions.

A second sample for acidic herbicides was then extracted. These samples were acidified (to pH 2 approx.) in the 4-litre bottles with 10 mL concentrated H_2SO_4. Surrogate standards for monitoring the recovery of the acidic herbicides were unavailable at the time of the study. Sample volume for the acidic extract was normally 20-litres. On occasions when DCM emulsion made 20-litre extraction impractical, the sample size was limited to 10-litres.

After completion of extraction, the extracts were decanted to separate 500 mL or 1-litre amber glass bottles fitted with teflon and foil-lined caps. DCM was drained from the GLSE mixing chamber, trap, and teflon column by repeated rinsing with extracted sample. Overlying water was subsequently poured off the extract to the extent possible. The extract samples were refrigerated until shipment to the National Water Quality Laboratory for analyses.

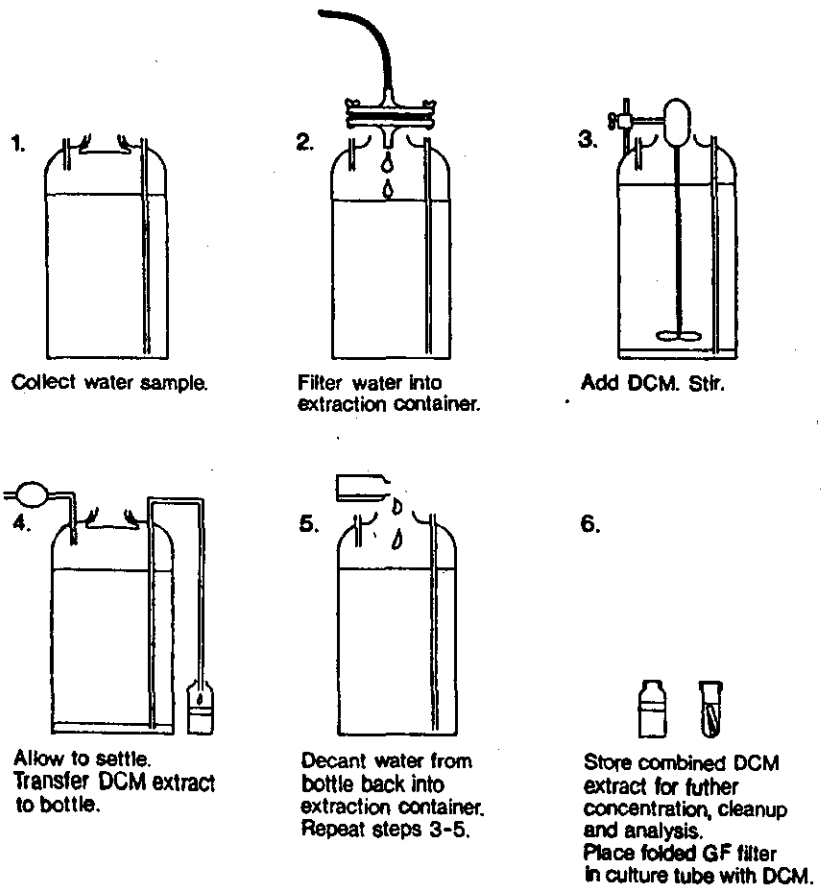
DCM lot numbers were recorded and clean DCM aliquots saved for submission as solvent and GLSE method blanks as required. Upon review of the analytical results, it was decided that blanks would not be submitted since one or more stations were free of residue detections during each longitudinal survey.

4.2.2.2 Pressure Container Sample Extractor (PCSE)

The Pressure Container Sample Extractor (PCSE) was developed by Fox at the National Water Research Institute (Fox 1986, 1991). The PCSE was tested at three stations on the Battle River (Hwy 611, d/s Camrose Ck, Unwin) during April 1990.

The PCSE, like the GLSE, is a liquid-liquid large sample extractor which uses DCM to pre-concentrate hydrophobic trace organics. The PCSE is not, however, a flow-through extractor, and may be thought of as a larger field variation of the separatory funnel extraction technique used in most laboratories. The PCSE offers certain advantages over flow-through systems including simplicity and ease of operation, the ability to perform multi-stage extractions, and the ability to do a series of extractions at different pH on a single sample. The PCSE is an alternative between more complex continuous flow-through extractors, and laboratory extraction of smaller volumes. A schematic of the PCSE method is presented in Figure 4.2.

Figure 4.2 Schematic of the Pressure Container Sample Extractor (from Fox 1986)



PCSE water samples were collected in pre-washed 20-litre stainless steel beverage containers. The samples were subsequently transferred to a Millipore stainless steel pressure container for extraction. Unfiltered samples were extracted (step 2 in Figure 4.2 was omitted) to retain consistency with previous surveys using the GLSE. Two samples were extracted, one at ambient pH for neutral herbicides and organochlorine/PCBs, and a second at pH 2 for acidic herbicides. The pH was adjusted in the pressure vessel by adding H_2SO_4.

Samples were extracted in two stages. An initial volume of 600 mL DCM was added to the sample in the pressure container, stirred at slow speed with a stainless steel and teflon mechanical stirrer for 15 minutes, then allowed to settle for 15 minutes. After settling, the first stage extract was forced from the extraction container by nitrogen pressure.

A 300 mL aliquot of DCM was then added, and the solvent-water mixture again stirred for 15 minutes and allowed to settle for 15 minutes. The second-stage DCM extract was purged under nitrogen pressure, and combined with the first-stage extract. Extracts were stored and handled according to methods used for the GLSE.

The same surrogate recovery standards used with the GLSE were added to the ambient pH sample from Unwin. Surrogate standards were not available for the two upstream samples, due to a shipping delay. A PCSE method blank using Milli-Q organic-free water (again fortified with surrogate standards) was extracted following the April survey. Beverage containers, pressure container, teflon tubing and extract bottles were cleaned according to pesticide protocols

(detergent and water, demineralized water, organic-free Milli-Q water, acetone-hexane, air dry) prior to the April survey. Between stations, the equipment was rinsed with organic-free water and DCM, and sealed with baked aluminum foil. All solvents used in the extraction and washing processes were pesticide grade.

An updated PCSE methodology (Fox 1991) recommends that samples be filtered using a Millipore 142 mm stainless steel in-line filter apparatus equipped with Gelman AE glass fibre filter. The filtrate is subsequently extracted using a two or three stage PCSE extraction. If desired, the filter can be submitted to the laboratory along with the water extract. Particulates on the filter paper are extracted in the laboratory, and the water and sediment extracts combined prior to analysis, to provide a 'whole water' extract with minimal DCM emulsion.

4.2.2.3 Grab Water Samples

Grab water samples from Unwin were collected, preserved, and handled according to Environment Canada sampling protocols (Water Quality Branch 1983). Samples were collected in 1.1 litre glass bottles, depth-integrated from near the center vertical. Neutral herbicide samples were preserved by addition of 15 mL chloroform; acidic herbicide samples were preserved with 5 mL concentrated H_2SO_4; organochlorine/PCB samples were not preserved. All samples were kept cool and protected from light during transit to the laboratory.

Grab samples were collected as part of the Prairie Provinces Water Board Interjurisdictional Monitoring Program. Attempts were made to coordinate collection dates with those of the Multi-Media Study, but field scheduling

requirements often made this impractical. The comparability of the grab and LSE results was thus reduced.

4.2.2.4 Bottom Sediment

To reduce the risk of sample contamination, all equipment used in the collection of bottom sediment samples for pesticide residues consisted of glass, teflon, or brass (Ekman dredge), which had been rinsed first in hexane and then in acetone. Samples to describe longitudinal variability within the basin were composites from the top one centimetre from at least ten dredges. All samples were frozen on dry ice immediately after collection and kept frozen during pre-analysis storage.

Results of pesticide analyses from longitudinal surveys indicated that most bottom sediment samples were devoid of measurable pesticide residues. In light of these results, and considering the cost and time involved in analyses, it was decided not to proceed with analyses of samples which were collected to describe intra-station horizontal and vertical distribution of pesticide residues. These samples have been banked at Alberta Environment's Millwoods Facility.

4.2.2.5 Suspended Sediment

Suspended sediment collection coincided with a major rainfall event in April 1990, which commenced the day before the survey began and continued for 48 hours. A Sedisamp System centrifuge was used for collection. The system consists of high speed Alfa-Laval industrial clarifier with stainless steel slotted-disc

centrifuge bowl (Envirodata Ltd. 1981). A submersible magnetic drive pump suspended near center stream (one meter below the water surface) delivered sample water to the centrifuge via 1.25 cm teflon tubing sheathed in 2.0 cm tygon tubing to provide additional durability. A 3500 watt generator provided power to the centrifuge and pump.

A stainless steel flow-splitter was mounted on the centrifuge bowl-housing to allow regulation of sample flow at approximately 5 litres/minute. The flow rate was checked every 30 minutes and corrected as necessary. An attempt was made to collect at least 100 grams of suspended material at each site. Total run times (a function of stream suspended sediment concentration, sample flow rate, and centrifuge recovery efficiency) varied from 3.5 to 8 hours.

Using a teflon spatula, samples were transferred from the centrifuge bowl to glass containers (with teflon-lined lids) immediately after centrifuge shutdown. Samples were refrigerated approximately two days, at which time subsamples for pesticide residues, metals, and particle size distribution were packaged. Samples for pesticide residue analyses were frozen on dry ice for shipment to the National Water Quality Laboratory.

Before the survey, all centrifuge sample contact parts, including pump, bowl, tubing, and fittings were washed with detergent, demineralized water, organic-free Milli-Q water, and rinsed with pesticide grade acetone, hexane, and dichloromethane. Between stations, the centrifuge bowl and slotted discs were washed with tap water, and rinsed with several volumes of organic-free water. Prior to commencement of sampling at each site, the pump and lines were flushed

with river water for several minutes and the centrifuge bowl was rinsed with river water before being housed in the centrifuge.

Samples of raw water and centrifugate were collected at each station to determine the efficiency of sediment recovery, which was estimated by comparison with analytical results for non-filterable residue (Section 4.4.2).

4.2.2.6 Aquatic Invertebrates

The equipment used in collection of aquatic invertebrates consisted of stainless steel, glass, or teflon rinsed with hexane then acetone, except the Nitex screens used for sorting, which were not solvent washed. Sampling methods were identical to those described for metals in Section 3. All samples were stored in wide-mouth pre-washed glass sample bottles with teflon cap-liners, and kept frozen until the time of analysis.

As a rule, the same taxa sampled for metal analyses were also sampled for analyses of pesticide residues. Hirudinea were submitted for pesticide analyses whenever the sample size was too small for both pesticides and metals. Based on the high frequency of non-detection in the June 1989 samples, the decision was made to analyze only a fraction of the samples collected in September 1989.

Analytical-size invertebrate samples required from two to ten person hours to collect, with the average collection time exceeding four person hours. A detailed discussion of the biological sampling methods used is presented in Section 3.2.4.

4.2.2.7 Aquatic Plants

Whole Potamogeton richardsonii plants (leaves, stems, and roots) were collected by hand and rinsed vigorously in river water to remove attached sediment before being frozen on dry ice. Mats of filamentous algae with some associated organisms were rinsed in river water to remove debris to the extent possible. All samples were stored in pre-washed wide-mouth glass sample bottles with teflon cap-liners, and kept frozen until analysis.

4.2.2.8 Fish

Forestburg Reservoir was chosen for fish collection for a number of reasons. The reservoir is located approximately 400 km. below the Battle River headwaters and is thus potentially recipient of a major percentage of the basin's agricultural drainage and municipal effluent. The size of the reservoir leads to a high probability of overwintering success and fish in the reservoir do not have access to downstream reaches, including the North Saskatchewan River. Fish were collected from an area immediately above the Highway 855 bridge, approximately 1 km above the Alberta Power generating plant.

Composite samples of liver and skinless axial muscle from five northern pike (Esox lucius) and five white suckers (Catastomus commersoni) were collected in November, 1989. Mixed mesh gill nets were used (60 meter net length, 3-5 inch mesh) and fishing effort totalled approximately 90 minutes. Dissection was done on-site immediately after collection. The working area and dissection equipment were rinsed with acetone and hexane. Tissue samples from each species were

composited, double wrapped in baked aluminum foil, and frozen on dry ice.

In April 1990, individual whole livers from 4 northern pike and 2 white suckers were collected (60 meters, mixed mesh 3-5 inch, fishing effort one hour). The dissection techniques and equipment were identical to those used in November.

4.2.3 Laboratory Methods

Detailed analytical methods are available on request from the National Water Quality Laboratory. Following are summaries of the analytical methods used during this study.

4.2.3.1 Acidic Herbicides in Water

Extraction: Source NWQL (a). Large volume acidic extracts were prepared in the field according to the methods outlined in Section 4.2.2. Grab samples are extracted in the laboratory in a two litre separatory funnel at pH less than or equal to 2. 100 mL dichloromethane is added and the funnel is shaken for one minute. After the layers separate, the DCM is removed to a 500 mL separatory funnel. The extraction step is repeated twice more using 2 X 50 mL DCM. From this point on in the analytical process, large volume extracts and grab extracts are handled identically.

Concentration: Excess moisture is removed upon transfer to a round bottom evaporation flask. Acetone (20 mL) is added to the flask for additional water removal. The solvents are evaporated to approximately 3 mL on a rotary evaporator. The extract is transferred to a 15 mL centrifuge tube, and washed with 3 x 2 mL acetone. The combined extract is evaporated under nitrogen to just dryness.

Esterification: 4.0 mL acetone, 200 mL 5% PFBBr and 30 uL of 30% K_2CO_3 are added to the centrifuge tube, the tube is stoppered and sealed with teflon tape, and allowed to react at 60 C. for three hours. The extract is evaporated to 1.0 mL under nitrogen. 4.0 mL hexane and 1.0 mL isooctane are added, mixed, and evaporated to 1.0 mL.

Cleanup: This step is required to remove co-extractives which react with PFBBr and interfere with the method. A micro column of de-activated silica gel topped with anhydrous sodium sulphate is wet with 5 mL hexane. Air voids are removed from the column. The 1.0 mL sample extract is applied to the column. The

from the column. The 1.0 mL sample extract is applied to the column. The centrifuge tube is rinsed with 4.0 mL 10% hexane, this washing added to the column. 8.0 mL of 75% toluene in hexane is collected in a clean centrifuge tube, and volume made up to 10.0 mL with isooctane. This fraction contains the PFB esters of all acidic herbicides with the exception of Picloram. 8.0 mL of 5% methanol in toluene is collected in a second centrifuge tube. Volume is increased to 10.0 mL with isooctane. This second fraction contains the PFB esters of picloram.

Chromatography: A gas liquid chromatograph utilizing split injector, dual capillary columns and dual electron capture detectors is used. Sample identity and quantification are by comparison with peak height and retention times of identically prepared analytical standards run on the same columns.

Confirmation: The acidic herbicides are confirmed by presence on the two columns. In cases of discrepancy between columns, and where concentration is sufficient, confirmation is done by negative ion GC/MS or MSD. When concentration is insufficient, additional concentration of extracts may be required for confirmation of identity. Non-confirmed results are not reported. The laboratory assigns a value of 95% confidence to compound identity of acidic herbicides, neutral herbicides, and organochlorine/PCBs. Somewhat lower confidence is generally applicable to quantification, which is affected by sampling and storage variables, and by recovery of laboratory and field standards.

4.2.3.2 Neutral Herbicides in Water

Extraction: Source NWQL (b) As per acidic herbicides, but at ambient pH, and with 3 x 100 mL dichloromethane used for grab samples. From this point, large volume extracts and grab extracts are handled identically. After water removal, the solvent is drained through a sintered funnel containing 5 cm anhydrous sodium sulphate. Filtrate is collected in a round bottom flask. An additional 50 mL dichloromethane is added to the second separatory funnel, passed through the drying column, and combined with the initial extracts.

Concentration: 10 mL isooctane are added to the combined DCM extracts, and the contents are reduced to about 3 mL on a rotary evaporator. 50 mL hexane or petroleum ether is added, and the extract is carefully evaporated to 3-5 mL.

Fractionation and Cleanup: Macro columns are prepared with 10% deactivated florisil topped with anhydrous sodium sulphate. The column is prewet with 100 mL hexane, which is discarded. The concentrated extract plus rinsings (4 x 1 mL hexane) is added to the column, eluted with 200 mL benzene/hexane (15:85) into a 500 mL roundbottom flask (fraction a: trifluralin, diallate, triallate). The column is eluted with 200 mL benzene/methanol (99:1) into a second flask (fraction b: barban, diclofop-methyl, benzoylprop-ethyl, atrazine, and metolachlor). 3 mL isooctane is added to each fraction, and fractions are evaporated to 3 mL on a rotary evaporator. Subsequent minicolumn elution may be required for additional cleanup.

Chromatography: Analyzed using dual capillary columns equipped with electron capture and nitrogen-phosphorous detectors. Identity is assigned by comparison with standards run individually under identical conditions.

Confirmation: The dual column technique is used for confirmation. When discrepancy arises and when concentration is sufficient, GC/MS or MSD are used for confirmation purposes. Non-confirmed results are not reported.

4.2.3.3 Organochlorines/PCBs in Water

Extraction: Source NWQL (c): Grab samples are extracted identically to the methods outlined for neutral herbicides. Large volume extracts are transferred to a glass separatory funnel, and swirled gently to separate emulsions. The solvent layer is drained through sodium sulphate into a round bottom flask. An additional 25 mL of DCM is used to further extract the aqueous layer, and added to the round bottom flask. An additional 2 x 25 mL DCM is washed through the sodium sulphate cake.

Concentration: 2.0 mL isooctane solution are added, and the extract is concentrated to 4 mL in a Goulden Evaporator. The extract is further concentrated to 2 mL under nitrogen. The extract is added to a centrifuge tube and made up to 2 mL with isooctane. Standards are added as controls for subsequent fractionation.

Fractionation and Cleanup: A silica gel column topped with sodium sulphate is prepared. This column is prewashed with 40 mL hexane. 1.0 mL of extract is added to the column (remaining extract is retained for GC/MS analysis). Fraction A is eluted with 40 mL hexane and Fraction B with 60 mL of 1:1 DCM/hexane. 1.0 mL isooctane is added to each fraction, and fractions are evaporated to 1 mL. Sulphur is removed by using pre-purified mercury. Additional calibration standards are added at this point, and the fractions are ready for GC/ECD analyses.

Chromatography: Chromatography is done on dual capillary columns with electron capture detectors. Identification and quantification are by comparison with retention times and peak areas of standards run under identical conditions.

Confirmation: As per neutral herbicides, dual column agreement is considered confirmation. GC/MS confirmation is undertaken if compound identity is questionable. Non-confirmed results are not reported.

4.2.3.4 Neutral Herbicides and Organochlorine/PCBs in Sediment and Biota

Extraction: (NWQL d) Sediments and biological samples are handled identically with the following exceptions. Ultrasonic extraction is used for sediments (20 gram initial sample), and polytronic extraction for biota (25 gram initial sample). Sediment results are reported as dry weight concentration which is calculated by determining moisture content on duplicate samples, while biota

results are reported as wet weight concentration.

Samples are weighed, and extracted using 100 mL acetone/hexane (1:1) in appropriate containers. After 3 minutes of extraction, sediments/biota are allowed to settle. A Celite column is prepared in a sintered glass funnel, washed with acetone/hexane (1:1). The initial extracts are collected in a round bottom flask under vacuum. Two additional extractions identical to the first are performed. After the third filtration, the sediment/biota are applied to the Celite column, washed with extract, and vacuum is applied to dryness.

Concentration: Extracts are reduced to 100 mL on a rotary evaporator, and transferred to a clean 500 mL separatory funnel. 100 mL organic-free water is added to the extract, shaken, and allowed to separate from the solvent phase. The aqueous layer is separated to a second separatory funnel, and extracted with DCM. The DCM is drained to the first funnel, and a second DCM extraction of the aqueous layer is done. The combined extracts are drained to a round bottom flask through sodium sulphate to remove water. Additional DCM is drained through the sodium sulphate, the combined extracts then reduced to 10 mL on a rotary evaporator. 50 mL hexane are added, and the extract is reduced to 3 mL on the rotovap.

Fractionation and Cleanup: A florisil column is used to elute the extract into two fractions using benzene/hexane (15:85) (Fraction A) and benzene/methanol (99:1) (Fraction B). Isooctane (3 mL) is added to each fraction, and the solvents are reduced to 3 mL on a rotary evaporator. Fraction A is then further fractionated on florisil mini-column with hexane (Fraction A1) and acetone/hexane (Fraction A2). Sulphur is removed from these two fractions using mercury.

Chromatography: The various fractions are analyzed on dual capillary columns with separate EC detectors. Identity is assigned by comparison with retention times of each compound analyzed individually under identical chromatographic conditions.

Confirmation: Confirmation is by dual column agreement. GC/MS or MSD confirmation is attempted dual column technique is non-conclusive. Non-confirmed results are not reported.

4.3 RESULTS AND DISCUSSION

4.3.1 Summary of Pesticide Results

Multi-media results are summarized in Table 4.5. Of the 38 target compounds analyzed, 21 were not detected in the five media investigated. Non-detected residues are tabulated in Table 4.6.

Twelve residues were measurable in water on at least one occasion. There were 99 detections in water during the study period with 83 occurring in large sample extracts and 16 occurring in the grab water samples collected at Unwin. The twelve residues found in water included seven acidic herbicides, three neutral herbicides, and two organochlorines (the alpha and gamma isomers of hexachlorocyclohexane, a-BHC and g-BHC).

A single compound was detected in sediments (30 bottom sediment and 3 suspended sediment samples were analyzed). Triallate, a neutral herbicide, was present in bottom sediments from five of six multi-media sites in June, 1989.

Biological tissues analyzed included eight taxa of aquatic invertebrates, two taxa of whole aquatic plants, and two species of fish muscle and liver. Seven residues were found in at least one of these biological media, including four neutral herbicides, two organochlorines, and polychlorinated biphenyls (total congeners).

Table 4.5 Summary of Multi-Media Pesticide Results

Compound	Detection Limit	Maximum [Conc]	Pos Dets/ Anals.	Pos Dets/Month 1989 M	J	J	A	S	O	N	D	1990 J	F	M	A
(1) Water (unfiltered large volume extracts from six sites) (ng/L)															
2,4-D	0.4	70.	15/33	5	4	6	-				-		-	-	
MCPA	0.3	5.1	12/33	1	5	6	-				-		-	-	
Gamma BHC	0.4	3.3	11/33	-	2	3	2				1		3		
2,4-DP	0.3	3.2	10/33	-	4	4	-				2		-		
Dicamba	0.3	1.7	8/33	-	3	5	-				-		-	-	
Bromoxynil	0.3	6.7	7/33	-	5	2	-				-		-	-	
Triallate	0.7	2.4	6/33	4	1	-	-				-		-	1	
Atrazine	3.0	13.	5/33	3	-	-	-				1		1		
Alpha BHC	1.3	1.97	3/33	-	-	-	-				-		3		
2,4,5-T	0.4	4.1	3/33	1	-	2	-				-		-	-	
2,3,6-TBA	0.4	2.2	2/33	-	2	-	-				-		-	-	
Trifluralin	0.4	0.42	1/33	1	-	-	-				-		-	-	
(2) Water (unfiltered 1.1 litre) (Battle River near Unwin) (ng/L)															
Alpha BHC	1.0	2.0	8/11	1	1	1	1	1	1	-	1	-	-	1	
Gamma BHC	1.0	4.0	5/11	1	1	1	1	-	-	-	-	-	-	1	
2,4-D	30.	90.	2/11	1	-	-	-	-	-	-	-	-	1	-	
2,4-DP	30.	60.	1/11	-	-	-	-	-	-	-	-	-	1	-	
(3) Sediments (Bottom:MJAS/89 and FA/90; Suspended:A/90) (ng/G dry)															
Triallate	0.2	0.88	5/33	-	5	-	-				-		-	-	
(4) Invertebrates (Surveys in June/89, Sep-Oct/89) (ng/G wet)															
Metolachlor	4.0*	10.6	5/33	-		5									
Triallate	2.0*	23.2	3/33	-		3									
Atrazine	4.0*	7.0	1/33	-		1									
pp-DDE	0.5*	0.94	1/33	1		-									
(5) Aquatic Plants (Collected August 1989, Filamentous Algae and Potamogeton richardsonii) (ng/G wet)															
Metolachlor	4.0*	40.	2/6			2									
Atrazine	4.0*	11.5	1/6			1									
Dieldrin	4.0*	4.0	1/6			1									
(6) Fish (Northern Pike, White Sucker: muscle and liver) (ng/G wet) (Collected November 1989, April 1990 Forestburg Res'r)															
Total PCB	25.*	247.	2/10				2						-		
Metolachlor	4.0*	4.6	2/10				-						2		
Triallate	2.0*	31.8	1/10				-						1		
Trifluralin	1.0*	1.0	1/10				-						1		
HCB	0.2*	2.8	1/10				1						-		

*detection limits for these compounds changed during the study period; pos dets/anal = positive detections/analyses

Table 4.6 Pesticide Residues not Detected in any Aquatic Medium

Group	Compounds
Acidic Herbicides	Silvex (Fenoprop), Picloram, MCPB, 2,4-DB
Neutral Herbicides	Diallate, Barban, Diclofop-methyl, Endaven
Organochlorine Insecticides	Heptachlor, Heptachlor epoxide, Aldrin, a-Chlordane, g-Chlordane, Endrin, a-Endosulphan, Mirex, b-Endosulphan, op-DDT, pp-DDT, pp-TDE, pp-Methoxychlor

4.3.2 Water

A compilation of detections in water, Alberta usage (usage data for 1981-1987 from Constable 1990), and residue mobility and persistence characteristics is presented in Table 4.7.

Two residues detected in water were high-use herbicides, with sales estimated at greater than 1000 tonnes active ingredient/annum in Alberta. MCPA was present in 12 water samples (maximum concentration 5.1 ng/L), and triallate in 6 samples (max. conc. 2.4 ng/L). The two herbicides have similar persistence, but MCPA is more mobile (i.e. is more leachable) (Table 4.7). Smith et al. (1981) (in McNaugton et al. 1990) estimated that over 50 per cent of crop land in the Prairies are treated with MCPA for broadleaf control, while approximately 30 per cent are treated with triallate for wild oat control.

Two of the herbicides found in water were from the second Alberta usage range, 500-1000 tonnes/annum. 2,4-D, the most frequently detected herbicide during this

Table 4.7 Pesticide Detections in Water, Alberta Usage, Relative Mobility and Persistence

Compound	Total[1] Detections	Alta Use[2] Ranking	Mobility[3]	Persistence[3]
2,4-D	17	2	2	4
gamma-BHC	16	3	3(b)	2(b)
MCPA	12	1	2	4
alpha-BHC	11	(a)	3(b)	2(b)
2,4-DP	11	4	nr	nr
Dicamba	8	3	1	3
Bromoxynil	7	3	2	4
Triallate	6	1	4	4
Atrazine	5	4	3	1
2,4,5-T	3	nil	nr	nr
2,3,6-TBA	2	nil	nr	nr
Trifluralin	1	2	5	2

1. Detections in large volume extracts and grab samples, a total of 44 samples. All samples were unfiltered water.

2. Derived from Constable (1990) (data for period 1981-1987)
   1. >1000 tonnes/annum
   2. 500-1000 tonnes/annum
   3. 100-500 tonnes/annum
   4. <100 tonnes/annum

3. From McNaughton et al (1990)

1=mobile	1=persistent 1-4 years
2=mobile	2=persistent 6-12 months
3=slightly mobile	3=persistent 2-6 months
4=slightly mobile	4=persistent 0-2 months
5=immobile	

Mobility was defined as the relative mobility in soils derived by comparing solubility (K_{ow}) and sorption (K_d) coefficients.

a isomer of gamma-BHC
b estimated from information in CCREM (1987)
nr not ranked (not registered for use and/or not marketed

study, was present in 17 of 44 water samples (maximum concentration 90 ng/L). Trifluralin was detected in one sample, at a concentration of 0.42 ng/L. Though more persistent than 2,4-D, trifluralin sorbs strongly to soils making it

virtually immobile once applied (Maguire et al. 1988). 2,4-D has been found in spring runoff near Swift Current, Saskatchewan (Nicholaichuk and Grover 1983). Nicholaichuk and Grover concluded that fall-applied 2,4-D can persist through the Canadian winter since degradation is reduced in cold and dry conditions.

Gamma-BHC (an organochlorine insecticide, commonly known as lindane) was found in 16 water samples (maximum concentration 4.0 ng/L), dicamba in 8 samples (max. conc. 1.7 ng/L), and bromoxynil in 7 samples (max. conc. 6.7 ng/L). Alpha-BHC, an isomer of gamma-BHC, was detected in 11 samples (max. conc. 2.0 ng/L). Between 100 and 500 tonnes of these compounds are applied annually in Alberta.

Dicamba is more mobile than the BHCs, while the BHCs are probably more persistent in water. The consistent detection of alpha-BHC and gamma-BHC in Western Canadian waters is well-documented. Integrated Environments (1989) reported the detection of alpha-BHC in 85 percent (and gamma-BHC in 27 percent) of surface water samples collected in the prairie provinces from 1971 to 1988.

Of the lower-use herbicides (under 100 tonnes/annum in Alberta), 2,4-DP (dichlorprop) was found in 8 water samples (max. conc. 60 ng/L), and atrazine in 5 samples (max. conc. 13 ng/L). 2,4-DP has properties similar to 2,4-D, with which it is often mixed for application (Ali and Hornford 1990). Phenoxy acid herbicides are characteristically mobile and non-persistent. Atrazine is somewhat less mobile but persistent. Atrazine is used for control of a variety annual broadleaf and grassy weeds in corn, which is tolerant to atrazine (CCREM 1987). It is also used industrially as a soil sterilant on non-croplands, and this may be the source in the Battle River basin. Atrazine is a common

contaminant in southern Ontario and U.S. surface waters, often measured at concentrations of 20 ug/L (CCREM 1987), and has been found in U.S. rainwater between 0.1 and >1.0 ug/L (Richards et al. 1987 in CCREM 1987).

Two compounds with negligible usage in Canada were detected. 2,4,5-T was found in 3 water samples (max. conc. 4.1 ng/L), and 2,3,6-TBA in 2 samples (max. conc. 2.2 ng/L). 2,4,5-T was de-registered in 1985 due to dioxin contamination in the formulation, and 2,3,6-TBA, though registered, has not been marketed in Canada in recent years (Agriculture Canada 1990). 2,4,5-T was reported present in 9 percent of Western Canadian surface water pesticide samples collected during 1971-1988 (Integrated Environments 1989).

Of the ten agricultural herbicides or insecticides which have consistent Alberta sales of over 100 tonnes/annum active ingredient, seven were detected in Battle River water during this study, two were not analyzed (glyphosate, difenzoquat), and one (dichlofop-methyl) was not detected.

Some of the variables which determine whether residues are likely to enter aquatic systems, and how they will act in those systems, were listed in Section 4.1.1. Of these variables, information describing the physical and chemical properties of residues is perhaps the most readily available. Laboratory measured solubility and adsorption coefficients (P_{ow} = 1-octanol/water partition coefficient, K_s = sediment-water distribution coefficient), when combined with characterizations of soil type, permit predictions of the leachability, mobility, and aquatic partitioning of residues. Other properties commonly determined in the laboratory include residue volatility, photodegradability, and

chemical/metabolic degradation rates, pathways, and products. With this information, estimates of residue persistence are possible.

Pesticide usage information, which is as important to the interpretation of monitoring data as residue characteristics, can be more difficult to gather. Pesticide sales data are protected as confidential business information. While total sales of active ingredients in each province are available from registrant surveys, accurate usage statistics for river basins or geographic areas are not generally available. Interpretation of monitoring results must take into account that the methods, timing, and extent of pesticide application can vary significantly within a basin from year to year, and from farm to farm. To maximize the information achievable from pesticide monitoring, usage surveys (i.e. questionnaires regarding application rates, timing, and field acreages) should be considered in monitoring design.

An attempt was made to correlate residue detections in water with the usage, relative mobility, and persistence data outlined in Table 4.7. There was little correlation between detection and usage ($r=-0.100$) or persistence ($r=0.323$). Some degree of correlation was apparent between detection and mobility ($r=0.522$). None of the correlations were significant at $p < 0.05$.

Pesticide residue detection frequencies using large sample extraction (GLSE and PCSE combined) and grab sampling techniques (Unwin site only) are displayed in Figures 4.3 and 4.4.

Figure 4.3 Detection Frequency in Water Using the GLSE and PCSE Methods at Six Multi-Media Stations

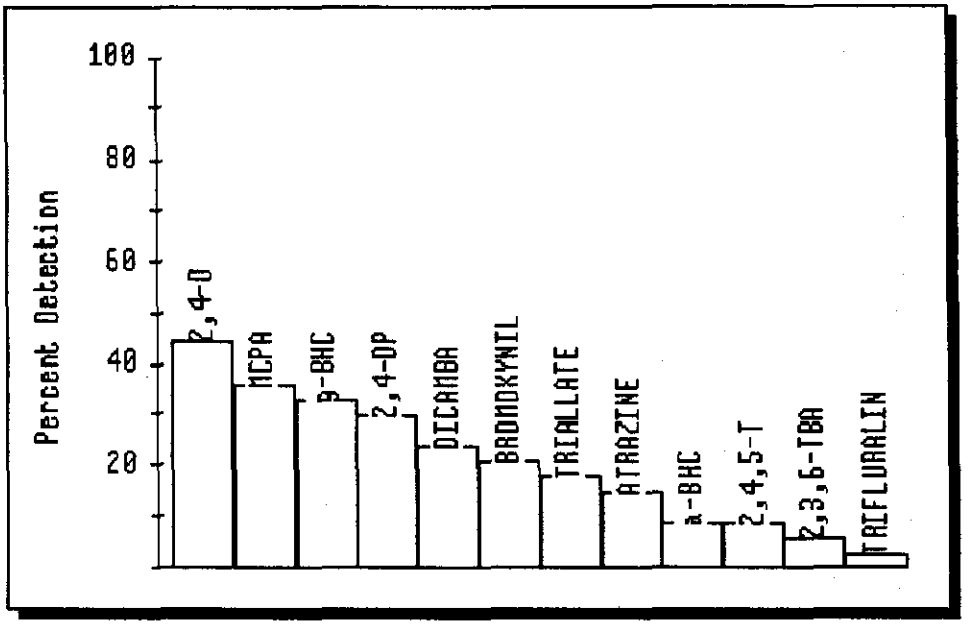
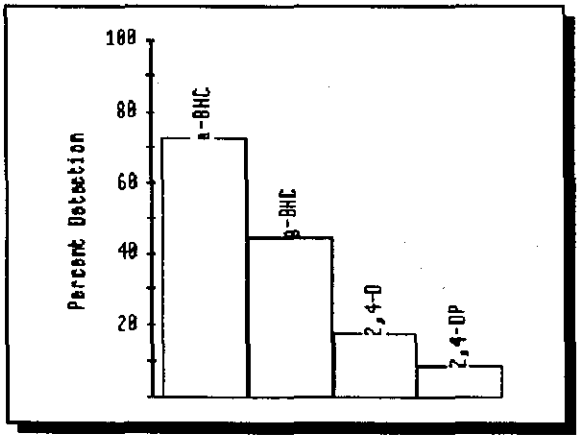


Figure 4.4 Detection Frequency in Grab Water Samples (Battle River at Unwin)



4.3.2.1 Seasonal Trends in Water

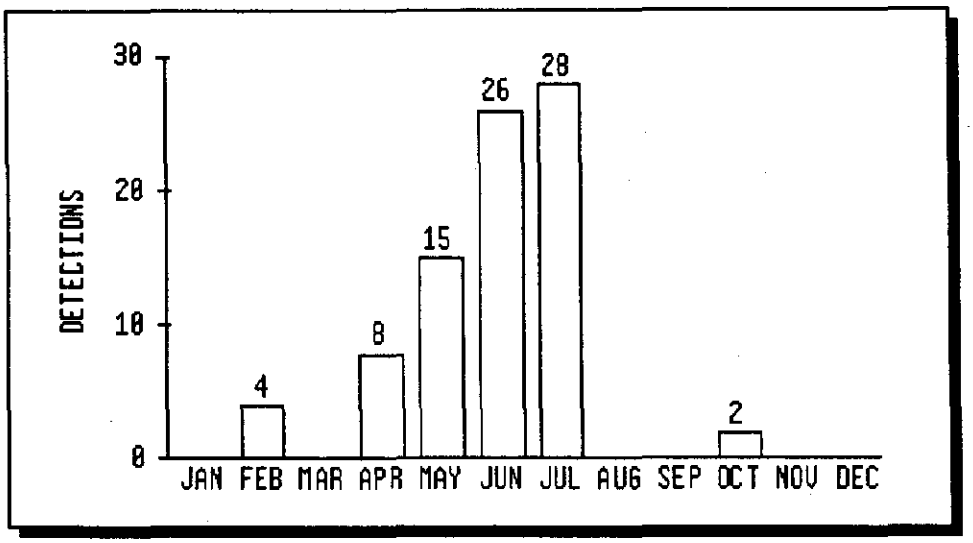
The majority of detections in large volume extracts occurred in May, June, and July (69 detections), coincident with the major application period. The May survey was undertaken early in the month during a moderately wet week, and it is possible that 2,4-D and triallate residues detected in water during that survey were from applications the previous fall. Only occasional detections were recorded in October, February, and April (14 detections) (Figure 4.5).

The majority of agricultural herbicides are applied during the early growing season, from May to early July, at either the pre- or post- weed emergence stage. Herbicides used for control of weeds in summer fallow are applied later, until approximately mid-summer. In recent years, fall herbicide application has become increasingly popular for the control of a variety of weeds in fields to be cropped or fallowed the next spring (Nicholaichuk and Grover 1983). Herbicides which can be fall-applied include triallate, trifluralin, bromoxynil, MCPA, and 2,4-D (Ali and Hornford 1990).

Of the organochlorine insecticides analyzed, only gamma-BHC is currently used agriculturally in Canada. It is used as a seed treatment for protection from wireworms. Most commercial formulations of gamma-BHC contain one or more fungicides such as captan, benomyl, maneb, etc. (Ali and Hornford 1990). Seed is uniformly covered with the lindane formulations in seed treatment equipment prior to spring (or fall) seeding.

The timing of industrial pesticide use can be variable, but the major application

Figure 4.5 Seasonal Variability in LSE Detection at Six Multi-Media Stations



period is the faster growing seasons of late spring to early summer. Deposition of atmospherically-borne residues might be expected to peak during the spring and early-summer rainy seasons. Contributions of atmospheric-source residues in snow during spring runoff may be significant as well (Gregor and Gummer 1989).

Pesticide entry into surface waters is most likely to occur at the time of application through aerial drift or overspraying of waters, or soon after application, in field runoff during rainfall events (e.g. numerous examples in CCREM 1987, Nicholaichuk and Grover 1983). Contamination of watercourses can also occur in spring snow runoff (Nicholaichuk and Grover 1983). In a review of a long-term Environment Canada pesticide monitoring data base, 2,4-D was found to be most frequently detected during March in the prairie provinces. This finding was likely related to snow melt runoff at times of low river discharge

(pers. comm. H. Block, Inland Waters Directorate). Block found that pesticide detections in the year-round monthly data base showed little seasonality beyond the March bias. Instead, detections appeared in apparently random 'pulses', supporting the conclusion that detections are related to the timing of both application and runoff events.

Alpha-BHC was detected consistently throughout the study period in grab samples from Unwin (8 of 11 samples). This frequency of occurrence (and lack of seasonality) is consistent with results from many other sites in Western Canada, and likely relates to alpha-BHC stability in the water column (CCREM 1987). The saturated structure is relatively stable to photodegradation. Volatilization and sediment adsorption are minimal.

4.3.2.2 Longitudinal Trends in Water

Detections of pesticides in GLSE and PCSE samples are arranged by station in Table 4.8 and presented graphically in Figure 4.6. A trend toward more frequent detection at the four downstream sites, located east of Highway 2, than at the two upstream sites is apparent (trend significant at $p < 0.01$).

Pesticide detections in LSEs are re-arranged in Table 4.9 to further illustrate longitudinal concentration trends. The table contains only the results of surveys for which individual residues were detected at three or more stations. The highest concentration recorded during each of those surveys is highlighted. Similar to detection frequency, there was a tendency for concentrations in water to be highest at one of the four downstream sites (significant at $p < 0.01$).

Table 4.8 Pesticide Detections in Large Sample Extracts at Six Multi-Media Stations

	Detections in Water during Study Period						
Pesticide	Hwy 611	Hwy 53	d/s Camrose	Hwy 872	Unwin	Mouth	Total
2,4-D	1	2	3	3	3	3	15
MCPA	2	1	2	2	2	3	12
Gamma-BHC	1	3	1	2	3	1	11
2,4-DP	2	0	3	2	2	1	10
Dicamba	1	1	2	1	1	2	8
Bromoxynil	1	0	1	1	2	2	7
Triallate	0	1	2	1	1	1	6
Atrazine	0	0	1	1	2	1	5
Alpha BHC	1	0	1	0	1	0	3
2,4,5-T	1	2	0	0	0	0	3
2,3,6-TBA	1	0	0	0	0	1	2
Trifluralin	0	0	0	1	0	0	1
# of Samples	6	5	6	5	6	5	33
Total	11	10	16	14	17	15	83

Figure 4.6 Longitudinal Distribution: Detections in Large Sample Extracts at Six Multi-Media Stations

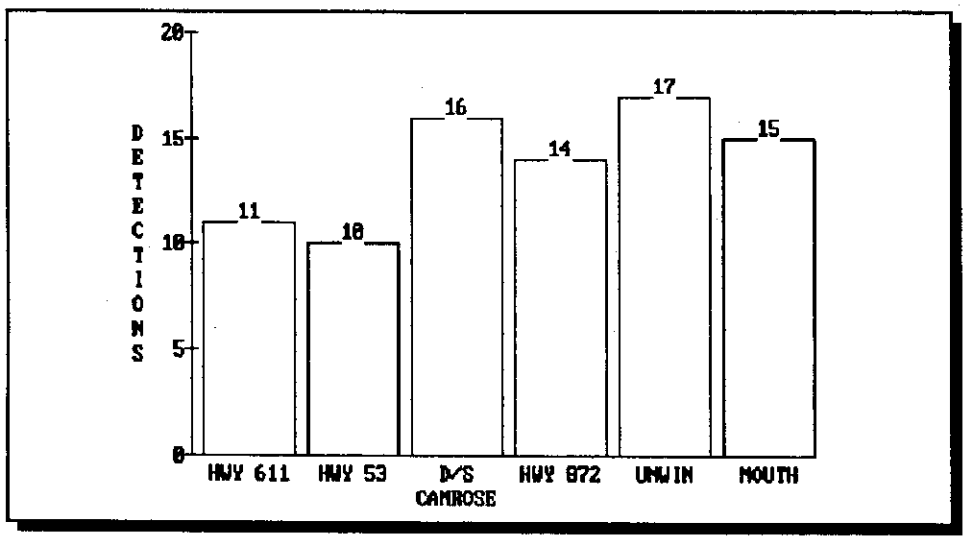


Table 4.9 **Pesticide Concentration in Large Volume Extracts (3 or more stations with positive concentration) (results in ng/L, max conc/survey highlighted)**

Pesticide/Survey	Hwy 611	Hwy 53	D/S Camrose	Hwy 872	Unwin	Mouth
2,4-D / May	ND	3.2	22.4	14.7	70.0	**74.4**
2,4-D / June	ND	ND	4.7	8.8	4.8	**18.9**
2,4-D / July	1.2	2.0	**6.6**	4.2	5.3	5.4
MCPA / June	0.5	ND	2.9	**5.1**	2.5	4.1
MCPA / July	0.47	0.53	2.1	**4.6**	**4.6**	2.0
Gamma-BHC / July	ND	0.97	ND	ND	**1.7**	0.6
Gamma-BHC / Apr	0.14	NA	0.81	NA	**3.27**	NA
2,4-DP / June	ND	ND	0.63	**1.60**	0.40	1.02
2,4-DP / July	0.30	ND	**0.84**	0.65	0.64	ND
Dicamba / July	ND	0.42	0.70	0.94	**0.99**	0.86
Bromoxynil / June	1.9	ND	2.2	0.72	2.0	**6.7**
Triallate / May	ND	ND	**2.44**	2.23	1.88	1.45
Atrazine / May	ND	ND	ND	7.68	12.13	**13.11**
Alpha BHC / Apr	0.5	NA	0.63	NA	**1.97**	NA

ND = not detected; NA = not analyzed

Downstream increased concentration might be expected for any constituent entering rivercourses from non-point sources. Longitudinal trends in pesticide monitoring data may be masked by factors such as sediment adsorption-sedimentation, degradation in the water column, and variabilities in farming practices, soil types, geography (i.e. slopes), weather, and timing of application. Certainly longitudinal trends detected in monitoring data (and in this study) should not be over-interpreted due to these factors, and the fact that sampling schedules are seldom matched with river time of travel.

4.3.2.3 Comparison of Results in Water with Water Quality Objectives

Concentrations of pesticide residues detected in water are compared with available water quality objectives in Table 4.10 and Figure 4.7. In all cases, the lowest (most protective) objectives which could be found in the literature are tabulated, regardless of jurisdiction or specific rationale (CCREM 1987, Water Quality Branch 1990).

The majority of results in water are three orders of magnitude or more below water quality guidelines or objectives providing protection for most-sensitive uses, either protection of freshwater aquatic life or of drinking water supplies. Alpha- and gamma-BHC concentrations in June/89 (6 ng/L total) and July/89 (6 ng/L total) were not far below the CCREM guideline of 10 ng/L (total of both isomers). This guideline is based on the sensitivity of cold water fish species to gamma-BHC.

Figure 4.7 Comparison of Pesticide Detections in Water to Sensitive-Use Water Quality Objectives

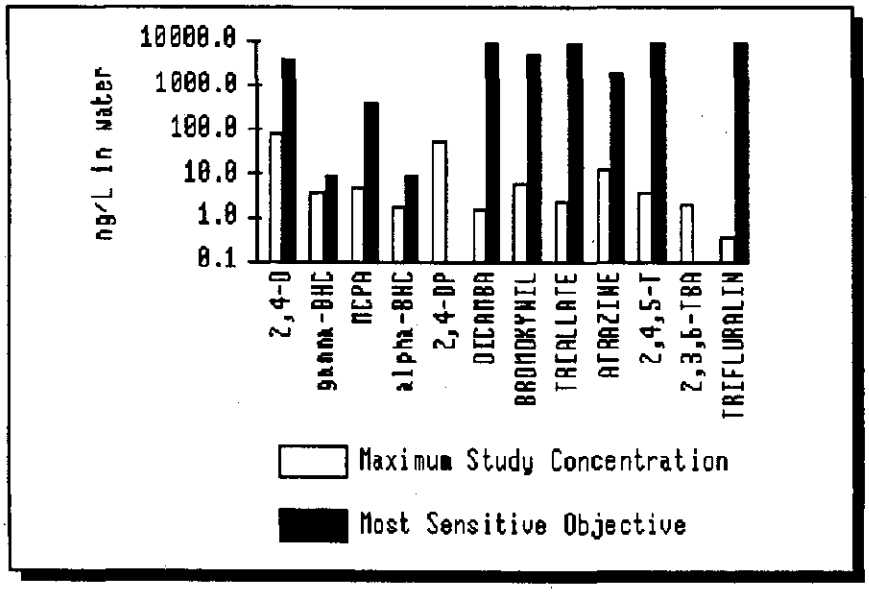


Table 4.10 Comparison of Pesticide Concentrations in Water To Sensitive-Use Water Quality Objectives

Compound	Total Detects[1]	Max Conc[2] ng/L	WQ Obj.[3] ng/L		Rationale[4]
2,4-D	17	90.	4000.	(a)	PAL
gamma-BHC	16	4.0	10.	(a)	PAL
MCPA	12	5.1	440.	(b)	DW
Alpha-BHC	11	2.0	10.	(a)	PAL
2,4-DP	11	60.	NA		
Dicamba	8	1.7	120000.	(c)	DW
Bromoxynil	7	6.7	5000.	(c)	DW
Triallate	6	2.4	230000.	(c)	DW
Atrazine	5	13.	2000.	(a)	PAL
2,4,5-T	3	4.1	280000.	(c)	DW
2,3,6-TBA	2	2.2	NA		
Trifluralin	1	0.42	35000.	(b)	DW

1. Detections in GLSE, PCSE, and grab samples (44 samples)
2. Maximum study concentration (April/89 to April/90)
3. (a) CCREM 1987; (b) NYSDEC 1986; (c) HWC 1987; NA=no objective found
4. PAL=protection of freshwater aquatic life; DW= maximum acceptable concentration in drinking water

4.3.3 Sediments

In addition to bottom sediments (six surveys) and suspended sediments (one survey) from the multi-media river stations, bottom sediments were also collected during June 1989 from three in-stream lakes (Battle Lake near Outlet, Driedmeat Lake Upper End, and Forestburg Reservoir Upper End) to determine whether these depositional areas might be acting as contaminant sinks. The results are presented in Table 4.5 and Appendix 4.8.

Detections in sediment were limited to a single residue during one bottom sediment survey. Triallate was present in 5 of 9 bottom sediment samples collected during June 1989 at concentrations ranging from 0.2 to 0.88 ng/G (dry weight). Longitudinal distribution in triallate detection and concentration was inconclusive. No residues were detected in suspended sediment samples.

Triallate, a carbamate herbicide used to control wild oats, can be applied in either the spring or fall (Ali and Hornford 1990). The carbamates are generally considered to be non-persistent (CCREM 1987). Triallate has been detected in bottom sediments of the LaSalle River in Manitoba at concentrations between 16.9 and 119 ng/G. (Therrien-Richards and Williamson 1988 in Constable 1991).

The extent to which a residue in water will adsorb onto a solid is a function of several factors. These include the physical and chemical characteristics of the sorbent (i.e. organic matter content), equilibrium factors, the surface area of the solid (i.e. particle size), and the nature and distribution of binding sites on the surface (Pagenkopf 1978 and Verschueren 1983 in CCREM 1987). Adsorption

is a complex phenomenon, which can occur through a number of mechanisms including weak attraction bonds such as Van der Waals forces, and chemisorption, which involves stronger chemical bonding (CCREM 1987). The values of K_s (ratio of sorbed to nonsorbed compound) can vary depending upon the nature of the sediment, and should be corrected for fraction of organic content in the sorbent material (CCREM 1987).

Triallate results and sediment characteristics are tabulated in Table 4.11. Correlations between triallate concentration and clay content ($r=0.12$) and percent organic matter ($r=0.01$) were weak and non-significant at $p < 0.05$.

Table 4.11 Bottom Sediment: Triallate Concentration, Particle Size, and Organic Matter Content

Station	Date 1989	[Triallate] ng/G dry	Sand %	Clay %	Silt %	Org C %	Org Matter %
Battle Lake	June 20	0.88	25.2	10.4	64.4	1.52	2.71
Hwy 611	June 20	<0.2	66.6	11.2	22.2	2.69	4.79
Hwy 53	June 21	0.2	86.6	7.2	6.2	0.34	0.61
d/s Camrose Ck	June 22	0.67	58.6	19.2	22.2	1.52	2.71
Driedmeat Lake	June 21	0.25	61.6	15.2	23.2	4.81	8.56
Forestburg Res.	June 23	<0.2	31.6	29.2	39.2	3.03	5.39
Hwy 872	June 23	0.26	90.6	6.2	3.2	0.60	1.07
Unwin	June 28	<0.2	95.6	3.2	1.2	<0.05	<0.09
Mouth	June 28	<0.2	95.6	4.2	0.2	<0.05	<0.09

As seen in Table 4.9, triallate was found in 4 of 6 six LSE water extracts from May 1989. The concentrations in water were between 1.4 and 2.4 ng/L at the four downstream multi-media stations, approximately 1/100 the concentrations in June bottom sediment. While the results may provide evidence of the movement of

triallate from the aqueous phase to the sediment, it is possible that triallate in the May 1989 LSEs originated in suspended sediment co-extracted with water (unfiltered water samples were extracted).

4.3.4 Biological Media

Summaries of pesticide results in biological tissues are presented in Table 4.12.

Table 4.12 Frequency of Detection in Biological Tissues

Compound	Detections / Total Samples		
	Aquatic Invertebrates[1]	Aquatic Plants[2]	Fish (liver)[3]
Metolachlor	5/33	2/6	2/10
Atrazine	1/33	1/6	ND
Triallate	3/33	ND	1/10
Trifluralin	ND	ND	1/10
pp-DDE	1/33	ND	ND
Dieldrin	ND	1/6	ND
Hexachlorobenzene	ND	ND	1/10
Total PCB	ND	ND	2/20

1. Sampled June 1989 and Sept 1989.
2. Sampled August 1989.
3. Sampled November 1989 and April 1990.

4.3.4.1 Aquatic Invertebrates

Aquatic invertebrate sampling coincided in June with the major pesticide application period, and in September with the time of year when invertebrate populations and lipid pools would be expected to be near maximum. Only one residue was detected in 21 taxon-specific June samples. pp-DDE was found in

Amphipoda from Highway 611, at a concentration of 0.94 ng/G whole body wet weight (analytical detection limit 0.5 ng/G wet weight). This primary metabolite of DDT is hydrophobic and persistent. Because of its solubility in lipids, pp-DDE is concentrated by organisms at all trophic levels (CCREM 1987). Bioconcentration factors as high as 10^6 have been reported for DDT isomers, and biomagnification occurs along the food chain (U.S. EPA 1979, 1980 in CCREM 1987). Whether biomagnification relates to progressive food chain transfer of organochlorines, or simply to the larger lipid pools present in higher organisms, remains uncertain (Day 1990).

All DDT products were de-registered from use in Canada in 1985. The terms of the de-registration allowed for the use and sale of existing stocks of selected rodent control products until December 31, 1990 (Agriculture Canada, 1990).

Literature reports of pesticide environmental concentrations in low trophic level organisms, including invertebrates, are limited. Day (1991), in a review of the literature on organochlorines in freshwater zooplankton, reported pp-DDE concentrations in marine zooplankton (North Sea, Mediterranean) from <0.5-94 ng/G (whole body wet weight). The presence of lipophilic pesticides in zooplankton (and aquatic invertebrates) may play a role in the redistribution of pesticides from deep sediment to the water column, where degradation would be expected to be more rapid (McNaught 1982, Harding 1986 in Day 1990).

Reports of pp-DDE in fish are more common in the literature. In 1981, northern pike and white suckers from Forestburg Reservoir were reported to have concentrations of pp-DDE as high as 1 ng/G in muscle, and 67 ng/G in fatty

to be found in Alberta fish despite the 1985 de-registration. Lockhart et al. (1990) reported that cutthroat trout taken in 1987 from lakes in Waterton Lakes National Park contained concentrations from 5-15 ng/G wet weight (total of pp-DDT, pp-DDD, pp-DDE, op-DDT). Donald (pers. comm. D. Donald, Inland Waters Directorate) reported pp-DDE concentrations in cutthroat and lake trout muscle from lakes in Waterton Lakes and Banff National Parks from 12-20 ng/G wet weight during 1991.

Due to the low frequency of detection in June, September invertebrates from three locations only were analyzed (Table 4.13).

Table 4.13 Pesticide Residues in Aquatic Invertebrates September, 1989

	Pesticide and Concentration (ng/G wet weight)		
	Downstream of		
Taxa	Hwy 611 89/9/26	Camrose 89/9/28	Unwin 89/10/03
Amphipoda	Met 10.6	Met 4.3	Met 4.1
Sphaeriidae	ND	----	ND
Simuliidae	----	----	----
Hirudinea	ND	Tri 5.3	----
Tubificidae	----	Tri 23.2	----
Chironomidae	----	----	----
Gastropoda	Met 8.9	Met 8.2	----
	Atr 7.0	----	----
Unionidae	----	----	Tri 3.9*

Met=Metolachlor; Tri=triallate; Atr=atrazine
---- Not Sampled
ND No Residues Detected
* duplicate samples analyzed (3.9 ng/G, <2.0 ng/G)

Metolachlor was found in 5 of 12 September invertebrate samples (all samples of Amphipoda and Gastropoda) at concentrations between 4.1-10.6 ng/G whole body wet weight. While metolachlor is used extensively in some parts of Canada (it was the most-used herbicide in Ontario in 1988), usage in Alberta is low and likely limited to irrigated areas where uses include control of a variety of weeds in corn, potatoes, soybeans, and sugar beets. It can be mixed with atrazine for control of weeds in corn crops (trade name Primextra). Use of metolachlor in the Battle River basin is probably very minimal. Literature information on metolachlor persistence and biota/sediment concentrations are limited (CCREM 1987). The compound has been detected in rainwater, coinciding with agricultural applications (Baker 1986 in Kent et al., 1991).

Three fall invertebrate samples contained triallate. The herbicide was found in Hirudinea and Tubificidae from downstream of Camrose, and in Unionidae from Unwin. Concentrations of triallate ranged between 3.9 and 23.2 ng/G whole body wet weight. A duplicate unionid clam from Unwin contained no detectable triallate (<2 ng/L). Triallate was the only pesticide to be detected in all aquatic compartments sampled: water, sediment, and biota.

Few literature references regarding triallate in biota could be found. In a survey of dry and permanent lakes in southern and central Saskatchewan, Donald (pers. comm. D. Donald, Inland Waters Directorate) found triallate in seven of twelve mixed zooplankton samples, at concentrations ranging from 2.3-10.2 ng/G (wet weight).

Atrazine was detected in Gastropoda from Highway 611 (7.0 ng/G wet weight).

Atrazine has been shown to accumulate in vascular plants and several animal species, though bioconcentration factors tend to be low and depuration relatively rapid (Trotter et al. 1990). The n-octanol/water partition coefficient for atrazine is in the range of 3×10^3 (Trotter et al. 1990).

The probable atrazine source in the Battle River basin is from weed control applications around oil and gas facilities. Atmospheric transport of atrazine can occur, and the residue has been found in rainwater samples in the Experimental Lakes Area of Ontario (Muir 1990 in Constable and Bharadia 1990).

Analytical detection limits for pesticide residues in sediment and biota were altered for most residues between the times of analyses of the June and September invertebrate samples (see Table 4.4) following a re-evaluation of the analytical method at the National Water Quality Laboratory. Any apparent seasonality in invertebrate results is likely invalidated by these changes.

Of the eight invertebrate taxa sampled during this study, Amphipoda and Gastropoda were the taxa of choice for pesticide monitoring in the Battle River based upon the frequency of pesticide detection, level of sampling effort required, physical size of specimens available, and their wide distribution.

4.3.4.2 Aquatic Plants

Residues detected in filamentous green algae and the macrophyte Potamogeton richardsonii are summarized in Table 4.14.

Table 4.14 Pesticide Residues in Aquatic Plants, August 1989

Taxa	Pesticide and Concentration ng/G (whole plant wet weight) Hwy 611 89/08/01	d/s Camrose 89/08/02	Unwin 89/08/03
filamentous algae	Atr 11.5 Met 10.9	ND	ND
Potamogeton richardsonii	Met 40.	ND	Diel 4.0

Met=metolachlor; Atr=atrazine; Diel=dieldrin; ND=no detections

Metolachlor was present in the algae and Potamogeton samples from Highway 611. The concentration in algae was similar to that measured in Amphipoda (10.6 ng/G) and Gastropoda (8.9 ng/G) at the same site. Aquatic invertebrates were sampled approximately two months after the aquatic plants. The metolachlor concentration in Potamogeton was approximately 4X higher than in algae. As mentioned in the preceding section, literature references regarding metolachlor concentrations in biota are limited. Metolachlor acts as a plant growth inhibitor, as do other acetamides, though the specific biochemical mode of action is poorly understood (Kent et al. 1991).

The concentration of atrazine in Highway 611 algae (11.5 ng/G) was similar to the concentration in found in Gastropoda (7.0 ng/G) at the site. Atrazine was not detected in Potamogeton samples, nor in algae from the two downstream stations. The finding of metolachlor and atrazine in both aquatic plants and invertebrates support the assumption that the compounds are used in the Battle River area, most notably in the upstream reaches of the basin, though usage information could not be found to support this assumption.

Dieldrin was present in Potamogeton from Unwin at a concentration of 4.0 ng/G wet weight (the analytical detection limit). The use of dieldrin in Canada is restricted to the treatment of subterranean termites by licensed applicators (Agriculture Canada 1990). Current usage in Alberta is likely negligible. Manufacture of dieldrin was halted in 1989, and use is being discontinued completely in a number of countries.

Dieldrin, like most organochlorine insecticides, is environmentally persistent. It sorbs to sediment and tends to accumulate in biota. Bioconcentration factors of approximately 10^4 in freshwater algae and 10^3 in fish have been reported (CCREM 1987). Dieldrin was detectable in only 7 of 4929 water samples collected by Environment Canada in western Canada during the 1970's and 1980's (Integrated Environments Ltd. 1989).

The presence of dieldrin in fish tissues has been reported commonly. The Alberta Environmental Centre (1982) reported dieldrin concentrations between <0.5 and 10 ng/G wet weight in white sucker lipid collected in Forestburg Reservoir during 1981. Lockhart et al (1990) reported that dieldrin concentrations in cutthroat trout from Waterton Lakes National Park ranged from 0.08 to 6.02 ng/G (wet weight whole fish) during 1987. Concentrations between <4 and 19 ng/G (wet weight muscle) have been found in lake trout muscle from Waterton Lakes and Banff National Parks (pers. comm. D. Donald, Inland Waters Directorate). Freshwater zooplankton from the Great Lakes were reported to contain dieldrin between <1. and 23 ng/G (lipid weight). References to dieldrin concentration in algae or vascular plants could not be found.

4.3.4.3 Fish

Residues were not detectable in November muscle samples from either fish species (Table 4.15). November liver samples from both species contained PCBs (total PCB congeners), with white sucker liver at 34.2 ng/G (wet weight), and northern pike liver at 247 ng/G. Hexachlorobenzene (2.8 ng/G) and trifluralin (1.0 ng/G) were present in northern pike liver.

Table 4.15 Pesticide Residues in Fish From Forestburg Reservoir November 1989 and April 1990

Species	Sample Type	Date	Residue - Concentration ng/G (wet weight)
White Sucker	Muscle (1)	November/89	No Detections
"	Liver (1)	"	PCB 34.2 ng/G
Northern Pike	Muscle (2)	"	No Detections
"	Liver (2)	"	PCB 247 ng/G HCB 2.8 ng/G Trf 1.0 ng/G
White Sucker	Liver (3)	April/90	No Detections
"	Liver (4)	"	No Detections
Northern Pike	Liver (5)	"	Tri 31.8 ng/G Met 4.5 ng/G
"	Liver (6)	"	No Detections
"	Liver (7)	"	Met 4.6 ng/G
"	Liver (8)	"	No Detections

(1) composite of 5 fish (3 male,2 female). Average fork length=400 mm
(2) composite of 5 fish (4 male,1 female). Average fork length=481 mm
(3) female, 430 mm
(4) female, 405 mm
(5) sex?, 550 mm
(6) sex?, 340 mm
(7) sex?, 680 mm
(8) sex?, 450 mm
PCB= total polychlorinated biphenyls; HCB=hexachlorobenzene; Tri=triallate; Met=metolachlor; Trf=trifluralin

No residues were detected in white sucker liver collected in April. Residues were present in 2 of 5 April northern pike liver, with one sample having triallate (31.8 ng/G) and metolachlor (4.5 ng/G), and the second metolachlor only (4.6 ng/G). These two northern pike livers were from the largest of the five fish sampled.

The inter-survey differences in liver PCB results is interesting since the fish from the two surveys were similar in size and taken from the same location. The differences may relate to seasonal changes in feeding habits, to short-term local contamination, or to sample handling and/or analytical error. PCBs are highly soluble in lipids, and PCB bioconcentration factors of 10^5 and higher have been reported for fathead minnows (Duke 1971 and Neely 1977 in CCREM 1987). Moore and Walker (1991) reported that most marine biota require one to several weeks to eliminate 50% of the lower chlorinated PCB congeners, and at least one to two months to eliminate higher chlorinated PCBs, though the depuration rates vary with species.

Concentration of PCBs in Forestburg Reservoir fish liver were similar to those reported for lake trout muscle (1991 fish) from Waterton Lakes and Banff National Parks (12 ng/G - 200 ng/G) (pers. comm. D. Donald, Inland Waters Directorate).

A 1981 survey of Alberta fish included results for PCBs in Forestburg Reservoir fish: white sucker muscle <0.5 - 200 ng/G; white sucker fatty tissue <0.5 - 4990 ng/G; northern pike muscle <0.05 - 20 ng/G; northern pike fatty tissue <0.05 - 4600 ng/G (Alberta Environmental Centre 1982). The 1981 results showed that intra-species variability in PCB concentration (one tissue type, one survey) can

be high.

The concentration of hexachlorobenzene in northern pike liver (2.8 ng/G) were similar to those reported for fish intestinal fat from Forestburg Reservoir in 1981: white sucker fat 2-9 ng/G; northern pike fat 1-14 ng/G (Alberta Environmental Centre 1982). Cutthroat trout from Waterton Lakes National Park were reported to contain 0.23-0.86 ng/G (whole fish wet weight) total chlorobenzenes in 1987 (sum of tetra-, penta-, and hexa-) (Lockhart et al. 1990).

In addition to PCBs and hexachlorobenzene, several other organochlorines were detected in Forestburg Reservoir fish during 1981 (Alberta Environmental Centre 1982). These included a-BHC, pp-DDE, chlordane and dieldrin, which were found frequently in intestinal fat. While it is probable that liver and intestinal fat residue concentrations are not fully comparable, the 1981 and 1989-90 fish results provide some evidence of decreasing organochlorine presence in Forestburg Reservoir fish.

Low metolachlor bioconcentration factors (6.5 to 9) have been determined for catfish muscle, with rapid depuration occurring upon withdrawal from exposure (Smith 1977 in Kent et al. 1991). Metolachlor was the only residue to be found in all biological compartments analyzed during the study. Maximum concentrations of metolachlor in each compartment were as follows: fish liver 4.6 ng/G; algae 10.9 ng/G; Potamogeton 40 ng/G; Amphipoda 10.6 ng/G; Gastripoda 8.9 ng/G. The results provide no evidence of metolachlor biomagnification.

Triallate, in addition to northern pike liver (31.8 ng/G), was found in aquatic

invertebrates (Hirudinea 5.3 ng/G, Tubificidae 23.2 ng/G, Unionidae 3.9 ng/G), bottom sediments (0.88 ng/G), and water (2.4 ng/L). Therrien-Richards and Williamson (1988) (in Constable 1991) reported concentrations of triallate in Manitoba fish between 3.3-9.2 ng/G wet weight. Constable (1991) reported rapid and complete depuration (in a few days) of triallate from rainbow trout after removal from exposure. The experimental bioconcentration factor for triallate in rainbow trout was determined to be 789 (Constable 1991).

Trifluralin, present at 1.0 ng/G in one northern pike sample, is moderately toxic to fish (rainbow trout, 24 hour LC_{50} 100-400 ug/L) (Macek et al. 1969 in McGuire et al. 1988). Trifluralin reaching aquatic ecosystems likely does so attached to soils, to which it sorbs strongly (McGuire et al. 1988). Depuration half-lives for trifluralin have been reported to be less than 2 months in various species of fish (Spacie and Hamelink, 1979 in McGuire et al. 1988).

4.4 METHODOLOGY CONSIDERATIONS FOR FUTURE MONITORING PROGRAMS

4.4.1 Large Sample Extractions

4.4.1.1 Standard Surrogate Recoveries

Ambient pH extracts for neutral herbicides and organochlorine/PCBs were fortified with standard organohalide surrogates to provide estimates of GLSE and PCSE method recoveries. During GLSE surveys, surrogates were prepared from concentrated stock solutions. Micro-syringe aliquots were diluted to 1000 mL in

methanol (pesticide residue grade), and metered into the sample continuously throughout the extraction process. The surrogates used were developed for organochlorine work on the Niagara River, and the methodology is often referred to as the 'Niagara protocol'.

Method recoveries for the first three GLSE were not calculated by the laboratory, since sets of laboratory analytical standards required to identify and quantify the Niagara protocol surrogates were not included with the analytical runs. Surrogates to monitor recovery of acidic herbicides were not available at the time of the study.

A second batch of Niagara protocol surrogates were used during the PCSE survey in April 1990. These were supplied by the laboratory pre-diluted in methanol and ready for field use. Using a volumetric flask, a 100 mL aliquot of the surrogate mixture was added to the PCSE prior to commencement of extraction.

GLSE and PCSE recoveries are presented in Table 4.16. The GLSE method recoveries were low, averaging between 10 percent and 24 percent. Recovery results for GLSE did not become available until very late in the study. This made it impossible to investigate causes of the low recoveries as the study progressed, and alter technique as required. Improved recoveries were reported for the PCSE sample at Unwin, between 72 and 89 percent. Recoveries for the PCSE method blank were more variable, from 23 to 111 percent.

Table 4.16 Surrogate Recoveries for Ambient pH Large Sample Extracts

Site	Date	Percent Recoveries d-BHC	1,3,5-TBB	1,2,4,5-TTBB	Method
Hwy 611	89/10/2	8	14	12	GLSE
Hwy 53	89/10/3	8	6	8	GLSE
d/s Camrose	89/10/3	ND	12	4	GLSE
Hwy 872	89/10/4	56	14	12	GLSE
Unwin	89/10/5	16	14	12	GLSE
Mouth	89/10/5	20	12	12	GLSE
October Survey Mean		18	12	10	GLSE
Hwy 611	90/2/5	17	40	21	GLSE
Hwy 53	90/2/6	16	22	29	GLSE
d/s Camrose	90/2/6	11	21	19	GLSE
Hwy 872	90/2/7	9	16	21	GLSE
Unwin	90/2/8	12	24	37	GLSE
Mouth	90/2/8	11	19	17	GLSE
February Survey Mean		13	24	24	GLSE
Unwin	90/4/25	89	84	72	PCSE
Method Blank	90/4/25	111	23	81	PCSE

While the recovery data indicate that the GLSE concentrations reported in Section 4.3 must be considered to be biased low (recovery corrections were not made), considerable confidence can be assigned to residue identity. All analyses were run on dual columns with dual detectors. Residue identities were not reported unless identically timed peaks matching those of the analytical standards appeared on both chromatographs. Low recovery does not hinder identification, given that concentrations remain above the analytical detection limit. Nor would it tend to increase the probability of false-positive results since analyte concentration and matrix complexity are simultaneously reduced.

The National Water Quality Laboratory uses a scheduled protocol for confirmation

of residue identity by GC/MS. Concentrations approximately one order of magnitude above those measurable on the electron capture detector are currently required for GC/MS confirmation. The residue concentrations in water during this study were too low for GC/MS confirmation. Further discussion of the recovery data is presented in Section 4.4.1.3.

4.4.1.2 Comparison of LSE and Grab Results from Unwin

Large sample extracts and grab samples from Unwin were not sample duplicates or splits, but were collected on different dates under separate monitoring programs. Logistical requirements made it impractical to coordinate the scheduling of the various field parties involved. Thus, full comparability of the two data sets is limited. Nevertheless, a comparison of grab sample detections with the corresponding LSEs (Table 4.17) can supplement the recovery data discussed in the previous section.

There were 10 detections (of 3 residues) in grab samples during months in which LSE surveys were conducted. GLSE concentrations of a-BHC and g-BHC were, in most cases, lower than the corresponding grab sample results. The PCSE results (April 1990) were slightly higher than the April grab samples for a-BHC and g-BHC. These results generally support the method recovery data presented in the previous section.

Large sample extract and grab sample detection limits reported by the NWQL for a-BHC and g-BHC were similar (see Table 4.17). This was due to the fact that grab sample detection limits were derived using test samples having relatively

Table 4.17 Comparison of Results for Large Sample Extracts and Grab Samples (Battle River at Unwin)

Date	Parameter	LSE ng/L	LSE Method	Grab ng/L
May/89	Alpha BHC	<1.3	GLSE	2.0
June/89	"	<1.3	GLSE	2.0
July/89	"	<1.3	GLSE	2.0
October/89	"	<1.3	GLSE	2.0
February/90	"	<1.3	GLSE	<1.0
April/90	"	1.97	PCSE	1.0
May/89	Gamma BHC	<0.4	GLSE	3.0
June/89	"	<0.4	GLSE	4.0
July/89	"	1.7	GLSE	4.0
October/89	"	0.4	GLSE	<1.0
February/90	"	<0.4	GLSE	<1.0
April/90	"	3.27	PCSE	3.0
May/89	2,4-D	70.	GLSE	50.

simple matrices. The LSE detection limits were determined with Niagara River water which has a more complex matrix in the area of the chromatograph in which a-BHC and g-BHC appear (pers. comm. G. Jamro, NWQL).

The detection of 2,4-D in the May grab sample (50 ng/L) and GLSE (70 ng/L) serves to confuse the recovery question. The results indicate that GLSE recoveries of acid extractives may have been more efficient than indicated for the neutral extractives.

4.4.1.3 Large Sample Extraction Assessment and Discussion

Goulden Large Sample Extractor

Poor GLSE recoveries likely resulted from loss of DCM due to emulsion during the extraction process. Emulsion can cause difficulty in performing DCM extractions, and is especially problematic in samples with high dissolved organic content and suspended particulates (pers. comm. D. Anthony, NWRI). Emulsion occurred during both neutral and acidic extractions, though the severity of the problem varied with from survey to survey. The acidic extraction tended to be particularly difficult, requiring that sample volumes be reduced to 10 litres on occasion.

Though the GLSE system has a teflon chip column and solvent trap to help break down emulsions and reduce solvent loss, it is probable that significant amounts of DCM were lost in the form of emulsive droplets. Between 1100 mL and 1200 mL of make-up DCM were needed to maintain solvent levels near the initial 150 mL level throughout extraction of 40 litres, considerably greater than that calculated from the solubility of DCM in water (1.6% w/w). There were occasions when the DCM level fell below 150 mL, requiring topping-up in mid-extraction. On a few occasions, the final extract volume was below 50 mL, and four extracts were discarded prior to analysis for this reason.

The GLSE used during this study was a model originally designed for water samples with simple organic matrices, such as rainwater or melted snow (pers. comm. D. Anthony, NWRI). It uses a highly efficient centrifugal pump for mixing the solvent and water phases. The combination of turbulent mixing, relatively small

unit capacity (i.e. short residence time), and 400 mL/minute flow-through rate, may not have allowed full separation of the phases at the point of sample outflow.

GLSE emulsion can be reduced in a number of ways (pers. comm. D. Anthony, NWRI): by the use of slower sample flow-through rates (250 mL/minute rather than 400 mL/minute); by use of newer GLSE prototypes which have larger capacity; by use of less-turbulent mixing with a mechanical stirrer rather than centrifugal pump, and; by clarification of the sample before extraction by centrifugation or filtration. Clarification of samples is considered by many to be a necessity to eliminate the co-extraction of contaminants from suspended sediment. The Battle River surrogate recoveries were much lower than those typically reported for samples which have been clarified (Neilson and Stevens 1988, Foster and Rogerson 1990).

LSE recoveries can also be improved by warming samples to approximately room temperature prior to extraction (pers. comm. D. Gregor, NWRI).

Pre-clarification, slower flow rates, and sample warming would be difficult to incorporate into routine pesticide monitoring programs, however. The GLSE procedure used required approximately four hours (two persons) to complete equipment setup, sampling, dual extractions, and cleanup. The addition of pre-clarification and slower extraction rate would add greatly to the time requirement.

GLSE performance studies have been done on several water types. In order of

increasing extraction difficulty, these water types were: drinking water and precipitation; estuarine water; freshwaters; pulp and paper mill effluents; and bog water (Anthony 1991). Difficulty in extraction was primarily related to the presence of dissolved organics. Suspended sediments were not a factor, since samples were pre-clarified.

Pressure Container Sample Extractor

Though the experience gained with the PCSE during this study was limited to a single survey, a number of advantages were apparent. The limited study data indicate that the PCSE is capable of achieving acceptable recoveries. Since the PCSE is not a continuous flow-through system, the method may be less vulnerable to DCM loss than the GLSE.

In terms of field applicability, the PCSE has the advantages of being relatively simple to operate, robust, and easy to clean. The PCSE method required approximately 2.5 hours for two 20 litre extracts, and was operable by a single individual. The addition of a third serial extraction would add approximately one hour to the time requirement. An additional advantage of the PCSE is that multiple extraction of a single sample at different pH can be accommodated. One possible disadvantage is that sample volume is restricted to the volume of the extractor vessel (approximately 20 litres). This can be overcome by combining two or more duplicate extracts.

The PCSE is at an earlier stage of development than the GLSE, and information concerning field evaluations of the PCSE are not currently available in the

literature. The PCSE is similar, though on a much smaller scale, to the aqueous phase liquid-liquid extractor (APLE), a 200 litre extractor developed by the Inland Waters Directorate in the early 1980s (McCrea and Fischer 1984). The APLE has been used in a number of applications in the Great Lakes region (McCrea et al. 1985).

Field and Laboratory Quality Control Considerations

The use of in-field extraction techniques requires a level of field quality control substantially greater than is normally associated with traditional monitoring. This includes the need to submit field method blanks, solvent blanks, and duplicate extracts at regular intervals, due to the hands-on nature of the techniques.

Alternatives to on-site extraction should be considered. Large samples can be filtered or centrifuged on-site, and extracted at a centralized field laboratory. This would help to maintain consistency in technique, since a limited number of well-trained personnel would undertake the extractions. It would also provide a cleaner and safer working environment (including fume hoods), and eliminate the cost of upgrading field vehicles. Holding time should be kept to a minimum to reduce adsorption to containers, but a 24-48 hour maximum should be acceptable and achievable in most situations. Delayed extraction would also allow time for samples to warm to room temperature, perhaps enhancing recovery efficiency.

Large sample extraction requires that a close relationship between the field and laboratory be maintained. Laboratory personnel can provide necessary technical

and interpretive advice, and are normally the source of recovery surrogates. The selection and acquisition of appropriate surrogates can be an involved process. Surrogates for the neutral and acidic herbicides are currently not available from the National Water Quality Laboratory, and routine in-field extraction of these compounds should not be considered until the surrogates become available. Ideally, the surrogate mixtures would include an array of ^{14}C-labelled analytes.

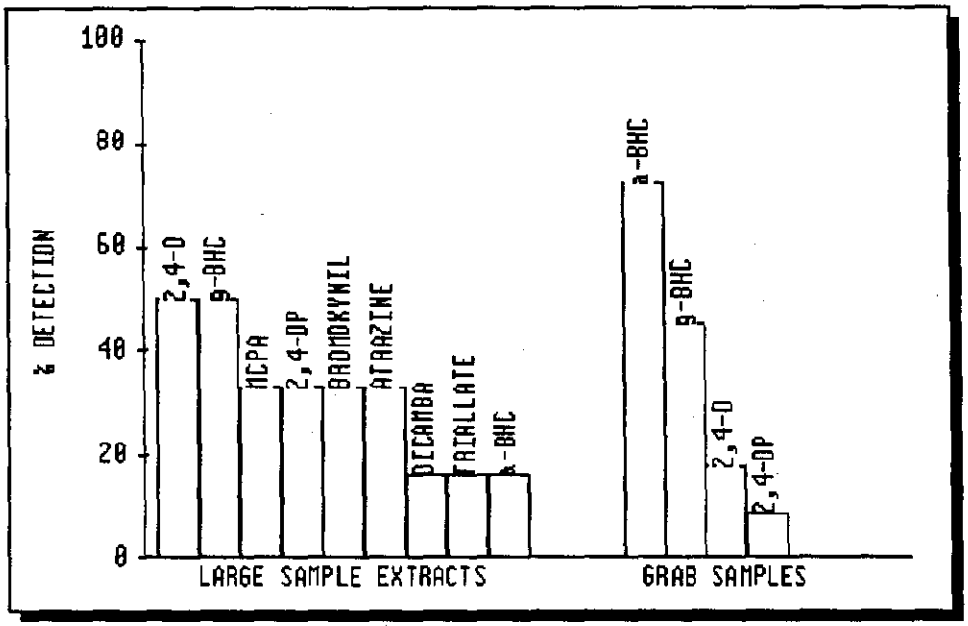
Cooperation with the laboratory is also necessary to achieve rapid analytical turnaround. Rapid turnaround is especially important in projects involving field extraction, as method recoveries and blanks must be reviewed in a timely manner to insure that the techniques being used are appropriate to the water types encountered.

Information Value: Large Sample Extracts verses Grab Samples

A further review of the Unwin data is useful in comparing the information provided by LSEs with that provided by grab samples (Figure 4.8).

Eleven grab water samples were collected at Unwin during the study. Four residues were present on at least one occasion: alpha-BHC (8 occasions), gamma-BHC (5), 2,4-D (2), and 2,4-DP (1), a total of 16 detections. In six large sample field extracts collected during the same period, nine residues were detected: 2,4-D (3 occasions), gamma-BHC (3), MCPA (2), 2,4-DP (2), bromoxynil (2), atrazine (2), dicamba (1), triallate (1), and alpha-BHC (1), a total of 17

Figure 4.8 Large Sample Extract and Grab Sample Detection Frequency (Battle River at Unwin)



detections.

Long-term Environment Canada pesticide monitoring programs in western Canada (Integrated Environments 1989) have produced conclusions similar to those derivable from the Unwin grab data. These conclusions may be summarized as follows: (1) alpha-BHC and gamma-BHC are commonly detected in Western Canadian surface waters, regardless of the season; (2) other organochlorines are rarely detected in water; (3) certain phenoxy acid herbicides (especially 2,4-D) are detected in water on occasion; (4) neutral herbicides are seldom detected in water, with the possible exception of atrazine in corn-growing areas.

The LSE results indicated the presence of residues which are detectable very infrequently at the one-litre detection limit (MCPA, bromoxynil, dicamba, and triallate). The lower LSE analytical detection limits allow the identification and quantification of baselines in water not possible with current analytical protocols and small volume samples.

Before implementing large sample extraction into water monitoring programs, however, an additional factor should be considered. While LSE methods can detect residues at lower concentration, the one-litre detection limits may already be below 'no-effect' concentrations. The objectives of each monitoring program should therefore be reviewed to determine whether reduced detection limits, with their added costs, are required.

4.4.2 Sediments

4.4.2.1 Sediment Collection Methodology

Bottom Sediment

The Ekman dredge was well-suited to bottom sediment sampling in the Battle River. Sediments ranged from organic muds to sands, and few stones or pebbles were present in most reaches. Collection was facilitated by shallow depth and low river velocity. The bottom was generally visible, and it was often possible to guide the dredge slowly to the bottom and to close the mechanism manually, causing little disturbance of the water and sediment interface. The average time for collection of a composite (10 dredge) bottom sediment sample was approximately 30 minutes for two persons.

Suspended Sediment

The Sedisamp System is field-portable, though heavy and cumbersome to transport, and can be used from low bridges, shores, or small boats. Updated models of the Sedisamp are available, which have solvent-rinsable stainless steel housing assemblies, allowing simultaneous collection of both clarified water and suspended particulate fractions for organic analyses. The operation manual for the Sedisamp model used in this study states that clarified water from this equipment should not be used for analyses, due to the possibility of contamination at the outlet side of the centrifuge.

The collection time for adequate sample sizes (100 grams is typically requested for multi-residue analyses) ranged from 3.5 to 8 hours (two persons). With lower suspended sediment concentration (1-3 mg/L) up to 24 hours of centrifugation can be required. A major drawback of the Sedisamp is the initial capital cost, which is about $25K.

Samples of raw water and centrifugate were collected to provide an estimate of centrifuge sediment recovery efficiency (Table 4.18).

Table 4.18 Sedisamp System Sediment Recovery Efficiency

Site		NFR (mg/L)	Extraction Efficiency (%)	Run Time (Hrs)
Hwy 611	raw water	12.4	>92.0	8
	centrifugate	<1.0		
d/s Camrose	raw water	52.6	97.0	7
	centrifugate	1.6		
Unwin	raw water	384.	96.0	3.5
	centrifugate	16.0		

Recovery efficiencies were similar to those published by Envirodata (1981) which states that the Sedisamp System provides >95% recovery of particles larger than 0.45 um. Recovery decreases proportionally with smaller grain size, though fine colloidals will be well-represented, since colloidals centrifuge as if they were larger particles. It is expected that very fine non-colloidals and organic materials would be under-represented using centrifugation, since these materials can have specific gravities similar to that of water.

Lower priced alternatives to centrifugation include passive samplers and filtration. Passive samplers, such as the Kenney sampler, are currently being tested in a number of locations (pers. comm. B.Kenney, NWRI). Potential problems with passive samplers include long collection times which may be sufficient to allow sample degradation, and the possibility that certain sediment size fractions may be non-proportionally represented.

Filtration is commonly used for analyses in sediment of parameters which can be micro-analyzed. Micro-analytical methods are not available for pesticide residues, however, and the collection of analytical weights by filtration would be time-consuming. It is practical to recombine extracts of filtered water and filter-bound sediments, for whole water analysis (Fox, 1991).

4.4.2.2 Sediments and Pesticide Monitoring: Assessment and Discussion

Bottom and suspended sediments provided the least information on pesticide presence of the media investigated. The findings of this study should not be considered conclusive regarding the applicability of sediments as candidate media

for future monitoring programs, however. Decisions on whether to include sediment analyses should be objective-specific and residue-specific.

Projects having ecosystem objectives would likely include bottom sediment residue analyses due to the intimate linkages between the sediments and biota and sediments and water. Projects requiring information on residue transport or loading to sensitive downstream areas might include analyses of the suspended sediment. The sediment-water partitioning tendencies and environmental persistence of pesticides are variable, and the assignment of sediment analytical lists should be based on these chemical and physical factors, together with accurate usage information. A brief review of the literature on pesticide residues in sediment follows.

Acidic Herbicides

The acidic herbicides were not analyzed in sediments during the study since analytical methods were not available at the National Water Quality Laboratory. The literature indicates a low likelihood of acidic herbicide presence in sediment (e.g. CCREM 1987). The phenoxy acid herbicides (2,4-D, MCPA, and related structures) are relatively water soluble, are predominantly anionic, and do not adsorb appreciably to sediment surfaces under normal aquatic conditions. Some sorption can occur at very low pH ranges to high organic soils.

Dicamba (a derivative of benzoic acid) is considered to be relatively non-persistent in terrestrial and aquatic environments. It does not sorb to particulate matter and is highly mobile. Despite its' mobility, dicamba likely metabolizes quickly to 3,6-dichlorosalicylic acid, which adsorbs strongly to

soils, before it can enter surface waters (Maguire et al. 1988). Maguire suggests monitoring for 3,6-dichlorosalicylic acid in sediment, as opposed to dicamba in water.

Maguire et al. (1988) reported that little information is available on bromoxynil mobility in soil, although its high water solubility should cause it to appear in the aqueous rather than the sediment phase. There is evidence which suggests that bromoxynil breaks down quickly in water to a brominated phenol and aliphatic sidechain (pers. comm. M. Constable, Environmental Protection).

The potassium salt of picloram, the most popular form of the herbicide marketed in Canada, is highly water soluble and relatively persistent in soil (Watson et al. 1989). Sorption is highest in acidic conditions, and is related to organic matter and clay content (an affinity for aluminum and iron oxides has been shown) (Norris 1970, Grover 1971, in CCREM 1987). Picloram has been shown to persist for several years in soils, and persistence is highest in cool dry conditions where microbial activity, the major cause of degradation, would be expected to be low (Watson et al. 1989). Picloram is used in the Battle River basin and in other areas of Alberta for control of leafy spurge.

Neutral Herbicides

Many of the neutral herbicides adsorb to sediment to some degree, with the extent of adsorption generally related to organic and clay content. Dichlofop-methyl degrades quickly in soils to diclofop, which binds very strongly to soils, removable only by hot alkali (Maguire et al. 1988). Trifluralin adsorbs very strongly to soils, and can persist from year to year. Degradation products of

trifluralin are diverse (Maguire et al. 1988).

Atrazine is persistent, and has been found in all aquatic compartments (CCREM 1987). There is evidence that atrazine adsorbs reversibly to sediment (Trotter et al. 1990). Newhook and Baril (1988), using persistence model results, reported that atrazine and metolachlor were the most persistent of the 26 top-selling pesticides in Canada (10 insecticides, 10 herbicides, 6 fungicides). The model predicted that atrazine should partition largely to water and metolachlor equally between water and sediment. Langlois and Sloterdijk (1988) reported detection of atrazine in 30 percent of sediment samples collected during one Quebec study.

Organochlorines and PCBs

Numerous studies have reported on the persistence of organochlorines/PCBs in bottom sediments (Frank et al. 1979, Holdrinet et al. 1978 in McCrea et al. 1985) and their presence in suspended sediments (Warry and Chan 1981, Kuntz and Warry 1983 in McCrea et al. 1985). The aqueous phase has been ignored to some extent in organochlorine studies due to the fact that concentrations in water tend to be below the detection limit for one or two litre samples (McCrea et al. 1985).

In a study of 17 organochlorines and PCBs in Niagara River, Great Lakes, and St. Lawrence River water (using the 200 L APLE extractor) and suspended sediments, McCrea et al. (1985) found that mirex and pp-DDE, when found, tended to be in the suspended sediment fraction, whereas a-BHC, g-BHC, dieldrin, endrin, pp-TDE, and trans-chlordane tended to be in the aqueous phase. A number of organochlorines (cis-chlordane, pp-DDT, pp-methoxychlor) were distributed between the suspended

sediment and aqueous phases. Between 90 and 100 percent of the total organochlorine and PCB contaminants present were found in the aqueous phase. A study of Niagara River water (Maguire and Tkacz 1989) suggest a more balanced partitioning of the organochlorines/PCBs between the aqueous and sediment phases.

A review of water-sediment partitioning information, Alberta usage, and Battle River results is presented in Table 4.19.

Table 4.19 Water-Sediment Partitioning Tendency of Selected Pesticide Residues

		Aquatic Compartment[2]				
	Alta Use[1]	Water	Dets	Sediment	Dets	
Compound	Ranking		Total[3]		Total[3]	References
2,4-D	2	++++	17/44	+	NA	CCREM (87)
MCPA	1	++++	12/44	+	NA	(a)
2,4-DP	4	++++	11/44	+	NA	(a)
2,4,5-T	nil	++++	3/44	+	NA	CCREM (87)
2,3,6-TBA	nil	++++	2/44	+	NA	(a)
MCPB	4	++++	0/44	+	NA	(a)
2,4-DB	4	++++	0/44	+	NA	(a)
Silvex	nil	++++	0/44	+	NA	CCREM (87)
Picloram	4	+++++	0/44		NA	Smith et al.(88)
Dicamba	3	+++	8/44	+++(b)	NA	CCREM (87)
Bromoxynil	3	+++++	7/44		0/33	Maguire et al.(88)
Triallate	1	+++	6/44	+++	5/33	Constable (91)
Atrazine	4	++++	5/44	+	0/33	CCREM (87)
Trifluralin	2		1/44	+++++	0/33	Maguire et al.(88)
Dichlofop-Me	3	+	0/44	++++(c)	0/33	Maguire et al.(88)
Metolachlor	4	+++	NA	+++	0/33	Newhook (88)
Diallate	nil	+++	0/44	+++	0/33	CCREM (87)
Barban	nil	+++	0/44	+++	0/33	CCREM (87)
Endaven	nil		0/44		0/33	No refs.
gamma-BHC	3	++++	16/44	+	0/33	CCREM (87)
alpha-BHC		++++	11/44	+	0/33	CCREM (87)
PCBs	nil	+++	0/44	+++	0/33	Maguire (89)
Other OCs	tr	+++	0/44	+++	0/33	Maguire (89)

1. Derived from Constable (1990), Alberta sales figures 1981-87:
   1. >1000 tonnes/annum; 2. 500-1000 tonnes/annum;
   3. 100-500 tonnes/annum; 4. <100 tonnes/annum
2. Estimates derived from reports in the literature:
   - ++++ only in this compartment
   - +++ largely in this compartment
   - ++ about half in this compartment
   - + seldom in this compartment
   - + traces in this compartment
3. Positive detections during Battle River Study. Total of LSE and grab samples, total of bottom and suspended sediment samples.

(a) reference not found, probably partitions similarly to other acidic herbicides

(b) breakdown product (3,6-dichlorosalicylic acid) adsorbs strongly to sediments

(c) degrades to dichlofop which adsorbs strongly to sediments

nil=not marketed; tr=trace marketed; NA=not analyzed

4.4.3 Biological Media

4.4.3.1 Biological Collection Methodology

The methods and relative difficulty in collection of biological tissue samples were discussed in detail in the Section 3.2.4.1. In order of sampling effort required in the Battle River, aquatic invertebrates > fish tissue > macrophytes and algae.

The collection effort for clean invertebrate samples varied with taxa, with the average collection requiring in excess of 4 person hours. Based on field criteria (abundance, size of organism, distribution in the basin, etc.) gastropoda were the preferred taxa (Table 3.6). Gastropoda samples required approximately 1.5 person hours for collection. The larger taxa (e.g. unionidae), while attractive in terms of collection of adequate sample size, were found to be poorly distributed through the basin. Samples of tubificidae and chironomidae were particularly difficult to collect (over ten person hours). It was not possible to produce samples free of sediment for these taxa, since they ingest sediments during feeding.

The effort required for collection of fish tissues was minimized due to the high population of northern pike and white sucker present in Forestburg Reservoir. These species were the only species caught during netting. Sample collection required one to one and a half hours with the 60 meter net used. Skinless muscle and liver dissections took approximately 10 minutes per fish. Fish were sized and sexed, but not aged.

Aquatic plant sample collection was rapid, and the two species chosen in the Battle River (Potamogeton richardsonii and filamentous algae) were relatively abundant throughout the basin. Whole Potamogeton plants were analyzed for pesticide residue though it is probable that concentrations in vascular plants vary in roots, stems, and leaves (this was the case with metals). The macrophyte samples were cleaned of sediments and other debris by rigorous rinsing in river water. This cleaning protocol was by its nature somewhat subjective, and amounts of foreign matter included with the samples may have varied. Cleaning of algae samples required more effort and including manual removal of visible debris before river rinsing.

Collection of biological tissue for analyses requires at least some biological expertise and if implemented in routine monitoring, staff training should be anticipated. Training requirements would likely be largest for the aquatic invertebrates with knowledge required to choose, locate, identify and sample various taxa. Training might also be necessary in the following: plant identification; fishing methods; and fish dissection and aging.

4.4.3.2 Biological Tissues and Pesticide Monitoring: Assessment and Discussion

A number of aquatic biological media have been used for monitoring organic chemicals in the surface waters of North America and Europe. Most biological work has been restricted, however, to surveys of organochlorines pesticides and PCBs or other industrial organochlorines, which tend to bioconcentrate and biomagnify, and can be very persistent. Biological databases for acidic herbicides and neutral herbicides, which are less lipophilic, are much less

common. The literature tends to agree that the aqueous phase should be the primary medium for monitoring of acidic herbicides.

Low frequencies of detection and concentration variability between taxa and species made it difficult to interpret biological results from the Battle River. Longitudinal and seasonal patterns tended to be unclear. This was partly due to limited numbers of detections and inter-species variability. Apparent seasonality in invertebrate results were thought to have been caused by a change in analytical detection limits.

An advantage of the use of invertebrates and aquatic plants is that their relative immobility may make description of longitudinal variability possible. Unfortunately, the rates with which plant and animal species take up, metabolize and depurate pesticide residues are all variable. Depuration rates tend to be higher (perhaps days to months) for many neutral herbicides, and lower for most organochlorines and PCBs (perhaps months or longer). Biological tissues cannot be expected, therefore, to time-integrate aqueous concentrations of all residues consistently, leading to the possibility of mis-interpretation of longitudinal and seasonal trends. References to residue uptake and depuration from all taxa or species are not available in the literature, and extensive basin studies may be required to choose preferred tissue types for routine monitoring.

Gastropoda was the preferred invertebrate taxa based upon ease of sampling. One or more residues were detected in Amphipoda, Hirudinea, Tubificadae, Gastropoda, and Unionidae. No residues were found in samples of Sphaeriidae. The study results did not indicate whether Potamogeton richardsonii or filamentous algae

were preferred plant media.

An advantage of the use of fish tissue is that fish trophic level, lipid content, and life expectancy should lead to higher concentration of persistent biomagnifying residues. This may have been reflected in the study results for fish liver, which was the only medium with detectable PCBs and hexachlorobenzene. Comparable fish residue databases are more common than for either invertebrates or plants. The work of Lockhart et al. (1990) and Donald (pers. comm. D. Donald, IWD) in the Rocky Mountain National Parks, and the Alberta Environmental Centre (1982) in various Alberta lakes, indicate that fish (whole fish, muscle, and abdominal fat were all analyzed) are a medium of choice for organochlorines and PCBs. A major disadvantage of using fish in river work is that their mobility, which can extend between basins, can make identification of contaminant sources difficult or impossible.

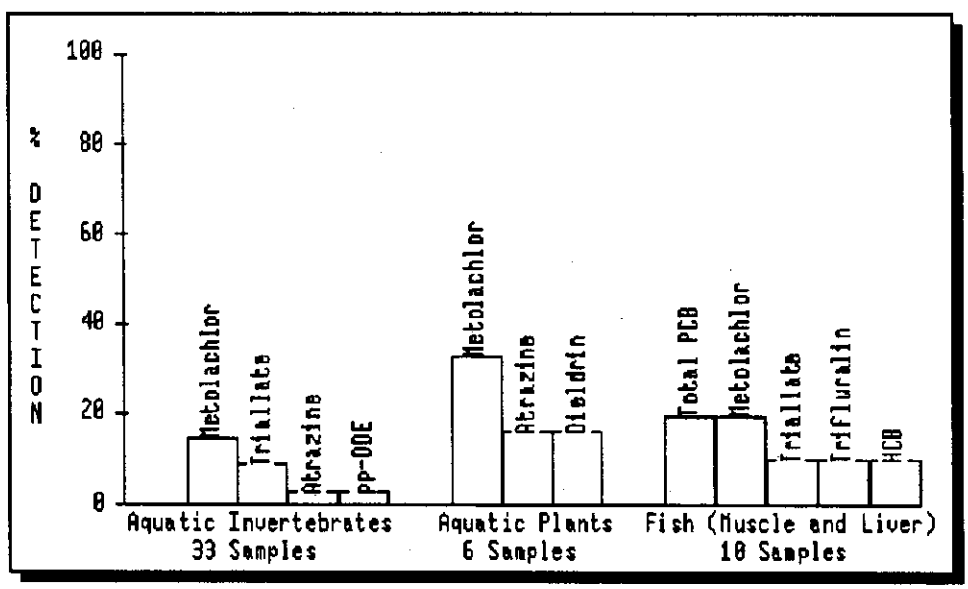
The study fish results showed variability between seasons (again the detection limit change may have been involved), between tissue type, between species, and within species. Based on number of detections, liver was the preferred medium during this study. Other studies have used a number of fish tissues for residue analyses, including bile, abdominal fat, blood, and whole fish. The choice of medium is largely dependant upon study objectives, but it is probable that concentrations of most residues are maximized in fatty tissues or organs.

The choice of fish species in most studies would out of necessity depend upon availability. If a choice of species is available, however, a piscivorous species should be chosen. Northern pike had higher residue concentrations than

white suckers during this study. Intra-species variability in pike liver concentrations were likely related to fish age and/or lipid content. Age, sex, and lipid analyses should accompany fish residue analyses to increase comparability within and between locations.

A comparison of the residues identified and frequency of detection in biological tissues is presented in Figure 9 (from Table 4.12). The differences in detection frequency between tissue types is probably not significant, considering the small number of samples analyzed. The information on neutral herbicide presence provided by the three tissue types is relatively consistent. This indicates that biological media may be interchangeable and that media of choice for neutral herbicides can be based largely upon availability and ease of sampling.

Figure 4.9 Frequency of Detection in Biological Tissues



4.5 SUMMARY AND CONCLUSIONS

Objectives of the Battle River Multi-Media Monitoring study included the investigation and selection of methods for sampling of various aquatic media, and the assessment and evaluation of these media in routine monitoring projects. Media sampled included water (traditional grab samples and large sample extracts), bottom sediment, suspended sediment, several taxa of aquatic invertebrates, macrophytes (Potamogeton richardsonii), algae (filamentous green), fish muscle, and fish liver.

The multi-residue study analytical list included 38 analytes (acidic herbicides, neutral herbicides, and organochlorine/PCBs). The analytical list included six of the highest selling Alberta herbicides, and eight of the top ten. 15 residues were detected in at least one medium; 21 residues were not detected in any medium. The study results for all media are summarized in Table 4.20.

Water

Twelve residues were measurable in water on one or more occasion. A total of 99 residue detections were reported in water samples. 83 detections occurred in 33 large sample extracts, of which 30 samples were Goulden extracts, and 3 samples were Pressure Container extracts. 16 residue detections were found in 11 grab samples collected at Unwin. The twelve residues found in water included seven acidic herbicides, three neutral herbicides, and two organochlorines. Compounds most frequently detected in water, ranked according to frequency, included, 2,4-D, MCPA, gamma-BHC, 2,4-DP, dicamba, bromoxynil, and triallate. Detections did not correlate significantly with usage data.

Table 4.20 Summary of Pesticide Results in Various Sampled Media (Residues Detected and Maximum Concentration)

Residues Detected	Water (LSE)	Water (Grab)	Sediments	Aquatic Invertebrates	Aquatic Plants	Fish Muscle	Fish Liver
	ng/L		ng/G(dry)	ng/G (wet weight)			
triallate	2.4		0.88	23.2			31.8
metolachlor				10.6	40.		4.6
atrazine	13.			7.0	11.5		
trifluralin	0.42						1.0
2,4-D	70.	90.					
MCPA	5.1						
2,4-DP	3.2	60.					
dicamba	1.7						
bromoxynil	6.7						
2,4,5-T	4.1						
2,3,6-TBA	2.2						
alpha-BHC	1.97	2.0					
gamma-BHC	3.3	4.0					
pp-DDE				0.94			
dieldrin					4.0		
Total PCB							247.
HCB							2.8

Several residues in water displayed significant seasonal (June and July maxima) and longitudinal variability (downstream increased concentration). A comparison of water results with water quality guidelines showed most concentrations to be well below sensitive-use guidelines. Alpha-BHC and gamma-BHC approached the CCREM (1987) guideline of 10 ng/L (total of both isomers) on two occasions.

The GLSE method recoveries were very low, between 10 and 24 percent. It was concluded that the poor recoveries resulted from DCM loss from the flow-through extractor caused by the design of the model available, and the specific technique (flow-through rate, stirring rate, extraction temperature) used. It was

concluded that the GLSE model used was inadequate for extraction of unclarified river water, and recommended that future LSE work should include clarification and warming of samples before extraction. Higher recoveries were reported for PCSE samples (72 to 89 percent), but the PCSE data was too limited to provide a valid comparison of the two methodologies.

The PCSE was thought to have a number of practical advantages to the GLSE in terms of ease of operation and field robustness. It was suggested that field lab extraction of GLSE samples was a practical alternative to in-field extraction.

Despite the poor GLSE recoveries reported during the study, the informational value of the GLSE results, based upon the ratio of residue detections in water to analytical cost, exceeded that from grab samples. The major disadvantages of LSE work involve the extra collection effort required, and the costs of significantly upgrading quality control protocols.

Sediments

Triallate was the only residue found in 30 bottom sediment samples (Ekmann dredge) and 3 suspended sediment samples (Sedisamp System). It was present in 5 bottom sediment samples from the June 1989 longitudinal survey. Of the aquatic compartments analyzed, the detection/cost ratio was lowest for sediments. No correlation was found between triallate concentration and particle size or percent organic matter. A comparison with the water results from May 1989 indicated the possibility of triallate movement from the aqueous to the sediment phase.

A review of the sediment literature indicates that some neutral herbicides (or their breakdown products) and the PCBs will sorb strongly to sediment. The majority of the neutral herbicides and organochlorine/PCBs partition between aqueous and sediment phases, though the older literature (pre-large sample extractor) indicates a strong preference of organochlorines/PCBs for sediment. The literature indicates that sorption of the acidic herbicides is minimal.

The Sedisampler was found to be a practical sampling tool. The time required for collection of adequate sample sizes (100 gm) can become excessive when suspended sediment concentrations are low. This should not usually be a factor in pesticide monitoring programs, however, as collection of suspended sediments would likely be timed according to spring runoff or major weather events.

The sediment recovery efficiency determined during this study was from 92 to 97 percent. The literature indicates that very small particles may be somewhat under-represented in centrifuge-collected samples. It was recommended that passive samplers should be considered for pesticide monitoring if ongoing testing shows their ability to collect representative and non-degraded samples.

Biological Tissues

Longitudinal and seasonal patterns in residue concentrations tended to be unclear, partly due to the limited number of detections, inter-species variability, and the lower frequency with which biological tissues were sampled during the study. The literature indicates a low likelihood of acidic herbicide presence in biological tissues, and they were not analyzed.

Comparable databases reported in the literature are largely restricted to organochlorine/PCBs, mostly in fish tissues. The study results and the results of several other Alberta organochlorine studies suggest that fish (piscivorous fish if available) are the medium of choice for organochlorine/PCBs, which are relatively persistent and tend to biomagnify up the food chain. Depending upon the specific monitoring objectives a number of fish tissues or organs might be used including whole fish, muscle, liver, bile, or abdominal fat.

The invertebrate, plant, and fish results for neutral herbicides were similar, with recurrent detection of metolachlor, atrazine, and triallate in at least two of the three media. This suggests that these media might be equally appropriate for monitoring of neutral herbicides.

Of the biological tissue types sampled, aquatic invertebrate samples were the most labour-intensive to find and clean in analytical quantity. Macrophyte sampling was the least labour-intensive. The literature states that uptake and depuration rates can vary between residues and between species. Thus it is unwise to assume that immobile media such as invertebrates or plants will provide consistent time-integration of aqueous conditions at a location. A disadvantage of the use of fish in river work is their mobility, making determinations of contaminant sources difficult.

Advantages and Disadvantages in the Routine Monitoring of Certain Media for Pesticide Residues

The advantages and disadvantages of the use of various media in monitoring of pesticide residues is outlined in the following table. The table is based on a number of factors including sampling requirements and availability, the study results for pesticide residues, and the available literature.

MONITORING ADVANTAGES	MONITORING DISADVANTAGES
WATER (GRAB SAMPLING)	
.ease of sampling .well established sampling protocols .analytical protocols at most labs .training and equipment requirements minimal .many comparable databases for water .guidelines available for most residues .water is most likely medium for acidic herbicides .field quality control protocols less important than for LSE .may be best method for a-BHC and g-BHC	.analytical detection limits are above most environmental concentrations .long delay between sampling and extraction often occur
WATER (LARGE SAMPLE EXTRACTION)	
.reduced analytical detection limits .no need for sample preservation .little delay between sampling and extraction .analytical cost identical to grab samples .can identify baseline and trends not achievable by grab sampling	.sampling and analytical protocols still being developed .method recovery surrogates for neutral and acidic herbicides unavailable .higher capital and field cost .require enhanced quality control .training requirements substantial .upgraded field vehicles needed for in-field extraction

MONITORING ADVANTAGES	MONITORING DISADVANTAGES
BOTTOM SEDIMENTS	
.some residues are persistent in deep sediment	.analytical protocols not available at all laboratories
.some residues sorb strongly to sediment (PCBs, some neutral herbicides)	.many herbicides do not sorb appreciably, Battle River results were largely negative
.ease of sampling	.relationships between bottom sediments and biota poorly understood
.low capital cost for collection	.adsorption is dependent upon particle size, organic content
.may provide time-integration of aqueous phase concentration for some residues	.adsorption is reversible for many residues
.lower sampling frequency than water likely acceptable	.persistence of different residues in sediment is highly variable
.sediment concentrations may have effects on associated biota	.particle size information required for site to site comparison
	.sampling locations should be located in deposition zones
	.proper substrate may not be available
	.fewer objectives or databases than for water
SUSPENDED SEDIMENTS	
.may be important transporting medium for some residues	.timing of sampling is critical, should be timed with runoff events
.when combined with TSS, can provides estimate of sediment loading of residues	.field methods are labour intensive
.sampling frequency likely low, timed with runoff or weather events	.high initial capital (Sedisampler)
	.particle size information required
	.impractical to collect adequate sample size when TSS is low
	.many residues do not sorb appreciably, Battle River results were negative
	.few comparable databases or objectives

MONITORING ADVANTAGES	MONITORING DISADVANTAGES
AQUATIC INVERTEBRATES	
.important food chain component .relatively immobile .longer life span than aquatic plant growing season .intimate relationship with bottom sediment .relatively wide distribution .likely provide some time-integration of aqueous concentration .provides data necessary for effect monitoring	.sampling is extremely labour intensive .comparable databases limited .percent lipid should be analyzed to enhance inter-taxa comparability .ingested sediment may complicate analyses and interpretation .uptake and depuration rates may vary between taxa .low concentrations expected for residues which biomagnify .analytical methods not available at all laboratories .Battle River data indicate high inter-taxa variability .one indicator taxon may not be available at all monitoring sites .sampling difficulties greatly increased in large rivers, or small rapid streams
AQUATIC PLANTS	
.immobile, may provide time-integration of growing season .easy of sampling .macrophytes intimately related to bottom sediments .slightly higher concentrations of detected residues than aquatic invertebrates during Battle study	.depuration rates poorly documented .high aqueous residue concentration may have effects on aquatic plants .few comparable databases or objectives .distribution of plant species may be limited .different plant parts may have varying concentrations of residues
FISH MUSCLE	
.implications to human health	.Battle River results were negative .literature generally reports that liver, abdominal fat, or whole fish may be preferable media for residue presence .fish mobility a problem in rivers .piscivorous species should be used

MONITORING ADVANTAGES	MONITORING DISADVANTAGES
FISH LIVER	
.higher concentrations than in muscle .high on the food chain, good medium for organochlorines/PCBs .provides a time-integration of aqueous concentrations for persistent	.can contaminate liver if gall bladder is broken .Battle River data indicate high intra- and inter-species variability .depuration rates vary residues .depuration rates may be high for some residues .concentrations dependant upon food supply and lipid content .fish are mobile, and residue origins may be difficult to determine .indicator species may not be available at all locations .fish should be weighed, sexed, aged to reduce intra- and inter-species variability

4.6 RECOMMENDATIONS

1. Large sample extractions should be undertaken on clarified water only, due to emulsion difficulties which tend to occur when suspended sediment and/or dissolved organics are present. The newer models of GLSE equipment should be acquired. These use a mechanical paddle stirrer and allow recovery of solution DCM. Samples should be warmed to room temperature prior to extraction.

2. Recovery surrogates for the neutral herbicides and acidic extractives should be developed as soon as possible. Ideally, these should be ^{14}C-labelled analytes.

3. A study to fully compare the recovery characteristics of the GLSE and PCSE methods under a variety of conditions is required before a decision on the preferred methodology should be taken.

4. An extensive quality control program of method blanks, spikes, and splits should be anticipated as an integral part of any future plans for wide-spread use of large sample extraction.

5. Consideration should be given to field-laboratory extraction of large sample extracts rather than in-field extraction for reasons of quality control.

6. Should routine methods become available, glyphosate (Roundup) and difenzoquat (Avenge) monitoring should be considered due to the substantial usage of these herbicides in Alberta.

7. Sediment detections were limited to a single compound (triallate). The data from this study and the literature suggest that monitoring of the ambient environment for current multi-residue parameter lists should concentrate on water and biological media, with lower emphasis on sediments. Any future sediment work should include documentation of particle size analyses, and in the case of bottom sediments, very precise documentation of collection location.

8. Though the Sedisamp System is considered to be practical for collection of suspended sediment, consideration should be given to the use of passive samplers for suspended sediment collection, due to their low cost and ease of use. This is dependent upon ongoing testing and evaluations proving that the samplers do not bias toward particular size fractions, and that degradation of residues during the collection period is not significant.

9. Future biological tissue monitoring should include the documentation of lipid content. This would increase inter- and intra-taxon comparability.

11. The study results and the availablility of comparable databases in the literature indicate that fish tissue are the preferred medium for monitoring of organochlorine/PCBs.

12. The study results indicate that large sample water extracts, invertebrates, plants, or fish may be applicable to the monitoring of neutral herbicides.

13. The literature suggests that acidic herbicides monitoring should be restricted to water.

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APPENDIX 4.8 DETAILED ANALYTICAL RESULTS

Name: Bromoxynil (3,5-dibromo-4-hydroxy benzonitrile)
(Trade names: Pardner; Buctril M (with MCPA))
Group: Acidic Herbicide, phenol derivatives
Uses: Broadleaf weed control in cereal crops.
Toxicity: Moderate acute mammalian toxicity. LD50 (rats) = 440 mg/Kg.
Highly toxic to fish.
Alberta Usage: Moderate (100,000-500,000 kg a.i./annum).
Registered for Canadian use in 1966.
Application Period: Seedling stage weeds (spring) or fall.
Objectives or Guidelines: HWC (87): 5 ug/L (IMAC drinking water)
Detection Limits: Water (1.0 liter): 30 ng/L (LSE): 0.3 ng/L
Summary of Results:

	1989					1990	
	May	June	July	Aug	Sep	Oct	Feb	Apr
WATER (results in ng/L)								
Hwy 611:	ND	1.9	ND			SD	ND	ND
u/s Ponoka:	ND	ND	ND			SD	ND	
d/s Camrose Ck:	ND	2.2	ND			SD	ND	ND
Hwy 872:	ND	0.72	ND			SD	ND	
Unwin:	ND	2.0	1.8			SD	ND	ND
Unwin (1 liter):	ND	ND	ND	ND	ND	ND	ND	ND
Battleford:	ND	6.7	1.8			SD	ND	

Name: 2,4-D (2,4 dichlorophenoxyacetic acid)
Group: Phenoxy Acid Herbicide
Uses: Broadleaf weed suppression in cereal crops; brush and weed control non-croplands; turf herbicide; restricted uses include conifer release, forest site preparation, and control of aquatic weeds.
Toxicity: Moderate acute mammalian. Acute oral LD50 (rats)=300-1000 mg/Kg.
Toxic to fish.
Alberta Usage: Large (>500,000 kg a.i./annum). Registration 1945-1954.
Application Period: During warm weather when vegetation is actively growing.
Can be fall-applied.
Objectives or Guidelines:
CCREM (87): 4.0 ug/L (protection of aquatic freshwater life)
HWC (87): 100 ug/L (MAC in drinking water, under review)
Detection Limits: Water (1.0 liter): 30 ng/L (LSE): 0.4 ng/L

Summary of Results:

	1989				1990		
	May	June	July	Aug	Oct	Feb	Apr
A. WATER (results in ng/L)							
Hwy 611:	ND	ND	1.2		SD	ND	ND
u/s Ponoka:	3.2	ND	2.0		SD	ND	
d/s Camrose Ck:	22.4	4.7	6.6		SD	ND	ND
Hwy 872:	14.7	8.8	4.2		SD	ND	
Unwin:	70.0	4.8	5.3		SD	ND	ND
Unwin (1 liter):	50.	ND	ND		ND	ND	ND
Battleford:	74.4	18.9	5.4		SD	ND	

Name: 2,4-DB (4-(2,4-dichlorophenoxy) butyric acid)
Other names: Embutox
Group: Phenoxy Acid Herbicide
Uses: Broadleaf weed control in cereal crops and pastures.
Toxicity: Low acute mammalian. Acute oral LD50(rats)=1960 mg/Kg.
Toxic to fish.
Alberta Usage: Low (<100,000 kg a.i./annum). Registered 1958.
Application Period: Post-emergent. Spring to late fall.
Objectives or Guidelines: Ontario (1984): 0.5 ug/L (Irrigation guideline)
Detection Limits: Water (1.0 liter): 50 ng/L (LSE): 0.4 ng/L
Summary of Results:

	1989					1990		
	May	June	July	Aug	Sep	Oct	Feb	Apr
A. WATER (results in ng/L)								
Hwy 611:	ND	ND	ND			SD	ND	ND
u/s Ponoka:	ND	ND	ND			SD	ND	
d/s Camrose Ck:	ND	ND	ND			SD	ND	ND
Hwy 872:	ND	ND	ND			SD	ND	
Unwin:	ND	ND	ND			SD	ND	ND
Unwin (1 liter):	ND	ND	ND	ND	ND	ND	ND	ND
Battleford:	ND	ND	ND			SD	ND	

Name: 2,4-DP (2-(2,4-dichlorophenoxy propanoic acid)
(Common name: Dichlorprop)
Group: Phenoxy Acid Herbicide
Uses: Broadleaf weed control in wheat and barley. Weed and brush control in industrial areas and roadsides. Usually applied with 2,4-D or other herbicides for broad spectrum weed control.
Toxicity: Moderate acute mammalian. Acute oral LD50(rats)= 800 mg/Kg.
Toxic to bees.
Alberta Usage: Low (<100,000 kg a.i./annum). Registered for Canadian use 1966.
Application Period: Late spring or early fall.
Objectives or Guidelines: N/A

Detection Limits: Water (1.0 liter): 30 ng/L (LSE): 0.3 ng/L
Summary of Results:

	1989					1990		
	May	June	July	Aug	Sep	Oct	Feb	Apr
A. WATER (results in ng/L)								
Hwy 611:	ND	ND	0.30			SD	3.2	ND
u/s Ponoka:	ND	ND	ND			SD	ND	
d/s Camrose Ck:	ND	0.63	0.84			SD	2.0	ND
Hwy 872:	ND	1.60	0.65			SD	ND	
Unwin:	ND	0.40	0.64			SD	ND	ND
Unwin (1 liter):	ND	ND	ND	ND	ND	ND	ND	ND
Battleford:	ND	1.02	ND			SD	ND	

Name: 2,4,5-T (2,4,5-trichlorophenoxy acetic acid)
Group: Phenoxy Acid Herbicide
Uses: Brush control and defoliant on rights-of-way and industrial areas.
Toxicity: Moderate acute mammalian. Acute oral LD50(rats)=500 mg/Kg.
Possible presence of p-dioxin as contaminant.
Alberta Usage: Not registered for use in Canada.
Registration period was 1948-1980. De-registered due to presence of TCDD in technical grade formulation.
Objectives or Guidelines: HWC (87): 280 ug/L (MAC in drinking water)
Detection Limits: Water (1.0 liter): 50 ng/L (LSE): 0.4 ng/L
Summary of Results:

	1989					1990		
	May	June	July	Aug	Sep	Oct	Feb	Apr
A. WATER (results in ng/L)								
Hwy 611:	ND	ND	1.2			SD	ND	ND
u/s Ponoka:	4.14	ND	0.85			SD	ND	
d/s Camrose Ck:	ND	ND	ND			SD	ND	ND
Hwy 872:	ND	ND	ND			SD	ND	
Unwin:	ND	ND	ND			SD	ND	ND
Unwin (1 liter):	ND	ND	ND	ND	ND	ND	ND	ND
Battleford:	ND	ND	ND			SD	ND	

Name: 2,3,6-TBA (2,3,6-trichlorobenzoic acid)
Other names: Trysben
Group: Phenoxy Acid Herbicide
Uses: Non-selective herbicide for broadleaf weed control, generally in non-crop areas.
Toxicity: Low-moderate acute oral mammalian toxicity. LD50(rats)=1500 mg/Kg.
Alberta Usage: Not marketed in recent years. Registered for Canadian use 1958.
Application Period: Spring
Objectives or Guidelines: N/A
Detection Limits: Water (1.0 liter): 30 ng/L (LSE): 0.4 ng/L
Summary of Results:

	1989					1990		
	May	June	July	Aug	Sep	Oct	Feb	Apr
A. WATER (results in ng/L)								
Hwy 611:	ND	2.2	ND			SD	ND	ND
u/s Ponoka:	ND	ND	ND			SD	ND	
d/s Camrose Ck:	ND	ND	ND			SD	ND	ND
Hwy 872:	ND	ND	ND			SD	ND	
Unwin:	ND	ND	ND			SD	ND	ND
Unwin (1 liter):	ND	ND	ND	ND	ND	ND	ND	ND
Battleford:	ND	1.04	ND			SD	ND	

Name: Dicamba (3,6-dichloro-2-methoxy benzoic acid)
(Trade name: Banvel)
Group: Acidic Herbicide, benzoic acid derivatives
Uses: Weed control when used alone. Used for brush control in mixes with 2,4-D.
Toxicity: Low acute mammalian. Acute oral LD50(rats) = 2600 mg/Kg. Low toxicity to fish; non-toxic to bees/birds.
Alberta Usage: Moderate (100,000-500,000 kg a.i./annum). Registered for Canadian use in 1963.
Application Period: Spring to early summer for broadleaf weeds in crops/pasture. Late summer for brush/summerfallow.
Objectives or Guidelines: HWC (87): 120 ug/L (MAC in drinking water)
Detection Limits: Water (1.0 liter): 30 ng/L (LSE): 0.3 ng/L
Summary of Results:

	1989					1990		
	May	June	July	Aug	Sep	Oct	Feb	Apr
A. WATER (results in ng/L)								
Hwy 611:	ND	1.4	ND			SD	ND	ND
u/s Ponoka:	ND	ND	0.42			SD	ND	
d/s Camrose Ck:	ND	0.4	0.70			SD	ND	ND
Hwy 872:	ND	ND	0.94			SD	ND	
Unwin:	ND	ND	0.99			SD	ND	ND
Unwin (1 liter):	ND	ND	ND	ND	ND	ND	ND	ND
Battleford:	ND	1.72	0.86			SD	ND	

Name: MCPA (4-chloro-2-methyl phenoxyacetic acid)
Group: Phenoxy Acid Herbicide
Uses: Control of broadleaf weeds in cereals and other crops.
Toxicity: Moderate acute mammalian toxicity. LD50(rats)=700-880 mg/Kg. Low toxicity to fish.
Alberta Usage: Large (>500,000 kg a.i./annum). Registered for Canadian use in 1984.
Application Period: Early spring or fall.
Objectives or Guidelines: NYSDEC: 0.44 ug/L (MAC Drinking Water) MCPA is currently under re-evaluation by Agriculture Canada.
Detection Limits: Water (1.0 liter): 30 ng/L (LSE): 0.3 ng/L
Summary of Results:

	1989					1990		
	May	June	July	Aug	Sep	Oct	Feb	Apr
A. WATER (results in ng/L)								
Hwy 611:	ND	0.5	0.47			SD	ND	ND
u/s Ponoka:	ND	ND	0.53			SD	ND	
d/s Camrose Ck:	ND	2.9	2.1			SD	ND	ND
Hwy 872:	ND	5.1	4.6			SD	ND	
Unwin:	ND	2.5	4.6			SD	ND	ND
Unwin (1 liter):	ND	ND	ND	ND	ND	ND	ND	ND
Battleford:	3.17	4.1	2.0			SD	ND	

Name: MCPB (4-(4-chloro-2-methylphenoxy) butanoic acid)
(Tropotox Plus=MCPB+MCPA)
Group: Phenoxy Acid Herbicide
Uses: Broadleaf weed control in cereal crops and pastures.
Toxicity: High acute mammalian toxicity. LD50 (rats)= 680 mg/Kg.
Alberta Usage: Low (<100,000 kg a.i./annum)
Application Period: Spring to early summer when plants are actively growing.
Objectives or Guidelines: Ontario (1984): 0.5 ug/L (irrigation guideline)
Detection Limits: Water (1.0 liter): 50 ng/L (LSE): 0.4 ng/L
Summary of Results:

	1989					1990		
	May	June	July	Aug	Sep	Oct	Feb	Apr
A. WATER (results in ng/L)								
Hwy 611:	ND	ND	ND			SD	ND	ND
u/s Ponoka:	ND	ND	ND			SD	ND	
d/s Camrose Ck:	ND	ND	ND			SD	ND	ND
Hwy 872:	ND	ND	ND			SD	ND	
Unwin:	ND	ND	ND			SD	ND	ND
Unwin (1 liter):	ND	ND	ND	ND	ND	ND	ND	ND
Battleford:	ND	ND	ND			SD	ND	

Name: Picloram (4-amino-3,5,6-trichloropyridine-2-carboxylic acid.
Trade name: Tordon)
Group: Acidic Herbicide, piclonic acid derivative
Uses: Brush control. Spot treatment on cultivated land, uility right-of-ways, pasture and rangeland to control specific weeds.
Toxicity: Low to moderate acute mammalian toxicity. Acute oral LD50(rats)=3000-10000 mg/Kg. Low toxicity to fish.
Alberta Usage: Low. (<100,000 kg a.i./annum).
Registered for Canadian use in 1964.
Application Period: Spring to early summer.
Objectives or Guidelines: HWC (87): 190 ug/L (MAC in drinking water)
Detection Limits: Water (1.0 liter): 50 ng/L (LSE): 0.5 ng/L
Summary of Results:

	1989					1990		
	May	June	July	Aug	Sep	Oct	Feb	Apr
A. WATER (results in ng/L)								
Hwy 611:	ND	ND	ND			SD	ND	ND
u/s Ponoka:	ND	ND	ND			SD	ND	
d/s Camrose Ck:	ND	ND	ND			SD	ND	ND
Hwy 872:	ND	ND	ND			SD	ND	
Unwin:	ND	ND	ND			SD	ND	ND
Unwin (1 liter):	ND	ND	ND	ND	ND	ND	ND	ND
Battleford:	ND	ND	ND			SD	ND	

Name: Silvex (Fenoprop, 2,4,5-TP) (2-(2,4,5-trichlorophenoxy) propanoic acid)
Group: Phenoxy Acid Herbicide
Uses: Broadleaf weed control in cereal crops, control of woody plants. Control of some 2,4-D resistant weeds.
Toxicity: Moderate acute oral mammalian. LD50(rats) = 650 mg/Kg.
Alberta Usage: Not registered for use in Canada. De-registered in 1980.
Objectives or Guidelines: CCREM (87): 10 ug/L (MAC in drinking water)
Detection Limits: Water (1.0 liter): 30 ng/L (LSE): 0.3 ng/L
Summary of Results:

	1989					1990	
	May	June	July	Aug	Sep	Oct	Feb	Apr
A. WATER (results in ng/L)								
Hwy 611:	ND	ND	ND			SD	ND	ND
u/s Ponoka:	ND	ND	ND			SD	ND	
d/s Camrose Ck:	ND	ND	ND			SD	ND	ND
Hwy 872:	ND	ND	ND			SD	ND	
Unwin:	ND	ND	ND			SD	ND	ND
Unwin (1 liter):	ND	ND	ND	ND	ND	ND	ND	ND
Battleford:	ND	ND	ND			SD	ND	

Name: Metalochlor (2-chloro-N-(2-ethyl-6-methylphenyl)-N-(2-methoxy-1-methylethyl) acetamide)
(Trade name: Dual, Primextra (with atrazine)
Group: Triazines and Acetanalides
Uses: Controls grasses and certain broadleaf species in corn and assorted vegetable crops. Broader spectrum weed control when combined with atrazine or other herbicides.
Toxicity: Very low mammalian toxicity. Acute oral LD50(rats)=2690-2780 mg/Kg. Slightly toxic to birds. Non-toxic to fish.
Application Period: Early spring, pre-planting or pre-emergent.
Objectives or Guidelines: HWC (1987): 50 ug/L (IMAC Drinking Water)
Detection Limits: Water: Analysis not available
Sediment, Biota: 25 ng/G (89), 4 ng/G (90)
Summary of Results:

	1989						1990	
	May	June	July	Aug	Sep	Oct	Feb	Apr
A. WATER (analysis not available at NWQL)								
B. BOTTOM SEDIMENT (results in ng/G)								
Battle Lake:		ND						
Hwy 611:	ND	ND		ND	ND		ND	ND/ND
u/s Ponoka:	ND	ND		ND				
d/s Camrose Ck:	ND	ND		ND	ND		ND	ND/ND
Driedmeat Lake:		ND						
Forestburg Res'r:		ND						
Hwy 872:	ND	ND		ND				
Unwin:	ND	ND		ND		ND	ND	ND/ND
Battleford:	ND	ND		ND				

Name: Atrazine (6-chloro-N-ethyl-N'-(1-methylethyl)-1,3,5- triazine-2,4-diamine)
Group: Triazines and Acetanalides
Uses: Control of grassy and broadleaf weeds in corn crops. General weed control in industrial/non-crop applications.
Toxicity: Very low acute mammalian. Acute oral LD50(rats)=1859-3080 mg/Kg. Very low toxicity to fish and birds. Persistent.
Alberta Usage: Low (<100,000 kg a.i./annum). Registered for Canadian use 1960.
Application Period: Spring pre-emergent.
Objectives or Guidelines: HWC (1987): 60 ug/L (IMAC Drinking Water)
Agriculture Canada initiated a re-evaluation of atrazine in 1988.
Detection Limits: Water (1.0 liter): 50 ng/L; (LSE): 3 ng/L
Sediment, Biota: 15 ng/G (89), 4 ng/G (90)

Summary of Results:

	1989						1990	
	May	June	July	Aug	Sep	Oct	Feb	Apr
A. WATER (results in ng/L)								
Hwy 611:	ND	IS	IS			ND	ND	ND
u/s Ponoka:	ND	ND	ND			ND	ND	
d/s Camrose Ck:	ND	IS	IS			ND	3.38	ND
Hwy 872:	7.68	ND	ND			ND	ND	
Unwin:	12.13	ND	ND			ND	ND	0.02
Unwin (1 liter):	SD	ND	ND	ND	ND	ND	ND	ND
Battleford:	13.11	ND	ND			ND	ND	
B. BOTTOM SEDIMENT (results in ng/G dry weight) (bolded results indicate suspended sediment)								
Battle Lake:		ND						
Hwy 611:	ND	ND		ND	ND		ND	ND/ND
u/s Ponoka:	ND	ND		ND				
d/s Camrose Ck:	ND	ND		ND	ND		ND	ND/ND
Driedmeat Lake:		ND						
Forestburg Res'r:		ND						
Hwy 872:	ND	ND		ND				
Unwin:	ND	ND		ND		ND	ND	ND/ND
Battleford:	ND	ND		ND				

Name: Barban (4-chloro-2-butynyl 3-chlorophenyl carbamate)
Group: Carbamate Herbicide
Uses: Wild oat control in cereal, oilseed, and legume crops.
Toxicity: Low acute mammalian. Acute oral LD50(rats)= 1300-1500 mg/Kg.
Alberta Usage: Not registered for use in Canada. Registration period 1960-1985.
Objectives or Guidelines: N/A
Detection Limits: Water (1.0 liter): 100 ng/L; (LSE): 7.6 ng/L
Sediment, Biota: 4 ng/G

Summary of Results:

	1989						1990	
	May	June	July	Aug	Sep	Oct	Feb	Apr
A. WATER (results in ng/L)								
Hwy 611:	ND	IS	IS			ND	ND	ND
u/s Ponoka:	ND	ND	ND			ND	ND	
d/s Camrose Ck:	ND	IS	IS			ND	ND	ND
Hwy 872:	ND	ND	ND			ND	ND	
Unwin:	ND	ND	ND			ND	ND	ND
Unwin (1 liter):	SD	ND	ND	ND	ND	ND	ND	ND
Battleford:	ND	ND	ND			ND	ND	
B. BOTTOM SEDIMENT (results in ng/G dry weight) (bolded results indicate suspended sediment)								
Battle Lake:		ND						
Hwy 611:	ND	ND		ND	ND		ND	ND/ND
u/s Ponoka:	ND	ND		ND				
d/s Camrose Ck:	ND	ND		ND	ND		ND	ND/ND
Driedmeat Lake:		ND						
Forestburg Res'r:		ND						
Hwy 872:	ND	ND		ND				
Unwin:	ND	ND		ND		ND	ND	ND/ND
Battleford:	ND	ND		ND				

Name: Diallate (S-(2,3-dichloro-2-propenyl)bis(1-methylethyl) carbamothioate
(Trade name: Avadex)
Group: Carbamate Herbicide
Uses: Wild oat control.
Toxicity: High mammalian toxicity. Acute oral LD50 (rats)= 395 mg/Kg.
Alberta Usage: Not registered for use in Canada. Registration period 1960-1976.
Objectives or Guidelines: N/A
Detection Limits: Water (1.0 liter): 100 ng/L; (LSE): 6.5 ng/L
Sediment, Biota: 4.0 ng/G

Summary of Results:

	1989						1990	
	May	June	July	Aug	Sep	Oct	Feb	Apr
A. WATER (results in ng/L)								
Hwy 611:	ND	IS	IS			ND	ND	ND
u/s Ponoka:	ND	ND	ND			ND	ND	
d/s Camrose Ck:	ND	IS	IS			ND	ND	ND
Hwy 872:	ND	ND	ND			ND	ND	
Unwin:	ND	ND	ND			ND	ND	ND
Unwin (1 liter):	ND	ND	ND	ND	ND	ND	ND	ND
Battleford:	ND	ND	ND			ND	ND	
B. BOTTOM SEDIMENT (results in ng/G dry weight)								
Battle Lake:		ND						
Hwy 611:	ND	ND		ND	ND		ND	ND/ND
u/s Ponoka:	ND	ND		ND				
d/s Camrose Ck:	ND	ND		ND	ND		ND	ND/ND
Driedmeat Lake:		ND						
Forestburg Res'r:		ND						
Hwy 872:	ND	ND		ND				
Unwin:	ND	ND		ND		ND	ND	ND/ND
Battleford:	ND	ND		ND				

Name: Diclofop-methyl (methyl-2-[4-(2,4-dichlorophenoxy)phenoxy]propionate)
(Trade names: Hoe-Grass, Glean, Torch)
Group: Neutral Herbicide
Uses: Control of wild oats and annual grasses in cereal, oilseed, and vegetable crops.
Toxicity: Low acute mammalian toxicity. Acute oral LD50 (rats)=2235 mg/Kg. Toxic to fish. Non-toxic to birds.
Alberta Usage: Moderate (100,000-500,000 kg a.i./annum). Registered for Canadian use in 1976.
Application Period: During active weed growth.
Objectives or Guidelines: HWC (1987): 9 ug/L (MAC Drinking Water)
Detection Limits: Water (1.0 liter): 50 ng/L; (LSE): 3.4 ng/L
Sediment, Biota: 1.5 ng/G (89), 4 ng/G (90)

Summary of Results:

	1989					1990		
	May	June	July	Aug	Sep	Oct	Feb	Apr
A. WATER (results in ng/L)								
Hwy 611:	ND	IS	IS			ND	ND	ND
u/s Ponoka:	ND	ND	ND			ND	ND	
d/s Camrose Ck:	ND	IS	IS			ND	ND	ND
Hwy 872:	ND	ND	ND			ND	ND	
Unwin:	ND	ND	ND			ND	ND	ND
Unwin (1 liter):	SD	ND	ND	ND	ND	ND	ND	ND
Battleford:	ND	ND	ND			ND	ND	
B. BOTTOM SEDIMENT (results in ng/G dry weight) (bolded results indicate suspended sediment)								
Battle Lake:		ND						
Hwy 611:	ND	ND		ND	ND		ND	ND/ND
u/s Ponoka:	ND	ND		ND				
d/s CamroseCk:	ND	ND		ND	ND		ND	ND/ND
Driedmeat Lake:		ND						
Forestburg Res'r:		ND						
Hwy 872:	ND	ND		ND				
Unwin:	ND	ND		ND		ND	ND	ND/ND
Battleford:	ND	ND		ND				

Name: Endaven (N-(3,4-dichlorophenyl)-alanine ethyl ester
(Common name: benzoylprop ethyl)
Group: Neutral Herbicide
Uses: Wild oat control in wheat and other cereals.
Toxicity: Moderate acute mammalian toxicity. LD50 (rats)= 1555 mg/Kg.
Alberta Usage: Not marketed in recent years.
Application Period: Tilling stage to second node stage
Objectives or Guidelines: N/A Registered for Canadian use in 1972.
Detection Limits: Water (1.0 liter): 25 ng/L; (LSE): 2.1 ng/L
Sediment, Biota: 1 ng/G (89), 2 ng/G (90)

Summary of Results:

	1989					1990		
	May	June	July	Aug	Sep	Oct	Feb	Apr
A. WATER (results in ng/L)								
Hwy 611:	ND	ND	ND			SD	ND	ND
u/s Ponoka:	ND	ND	ND			SD	ND	
d/s Camrose Ck:	ND	ND	ND			SD	ND	ND
Hwy 872:	ND	ND	ND			SD	ND	
Unwin:	ND	ND	ND			SD	ND	ND
Unwin (1 liter):	ND	ND	ND	ND	ND	ND	ND	ND
Battleford:	ND	ND	ND			SD	ND	
B. BOTTOM SEDIMENT (results in ng/G dry weight)								
Battle Lake:		ND						
Hwy 611:	ND	ND		ND	ND		ND	ND/ND
u/s Ponoka:	ND	ND		ND				
d/s Camrose Ck:	ND	ND		ND	ND		ND	ND/ND
Driedmeat Lake:		ND						
Forestburg Res'r:		ND						
Hwy 872:	ND	ND		ND				
Unwin:	ND	ND		ND		ND	ND	ND/ND
Battleford:	ND	ND		ND				

Name: Triallate (S-(2,3,3-trichloro-2-propenyl)bix(1-methylethyl) carbamothioate)
(Trade name: Avadex BW)
Group: Carbamate Herbicide
Uses: Wild oat control in cereal crops.
Toxicity: Low acute mammalian. Acute oral LD50(rats)= 1675-2165 mg/Kg. Slightly toxic to fish. Non-toxic to birds.
Alberta Usage: Large (>500,000 kg a.i./annum). Registered for Canadian use in 1962.
Application Period: Spring and fall.
Objectives or Guidelines: HWC (1987): 230 ug/L (MAC in drinking water)
Detection Limits: Water (1.0 liter): 10 ng/L; (LSE): 0.7 ng/L
Sediment, Biota: 0.2 ng/G (89), 2 ng/G (90)

Summary of Results:

	1989						1990	
	May	June	July	Aug	Sep	Oct	Feb	Apr
A. WATER (results in ng/L)								
Hwy 611:	ND	IS	IS			ND	ND	ND
u/s Ponoka:	ND	1.30	ND			ND	ND	
d/s Camrose Ck:	2.44	IS	IS			ND	ND	0.29
Hwy 872:	2.23	ND	ND			ND	ND	
Unwin:	1.88	ND	ND			ND	ND	ND
Unwin (1 liter):	SD	ND	ND	ND	ND	ND	ND	ND
Battleford:	1.45	ND	ND			ND	ND	
B. BOTTOM SEDIMENT (results in ng/G dry weight) (bolded results indicate suspended sediment)								
Battle Lake:		0.88						
Hwy 611:	ND	ND		ND	ND		ND	ND/ND
u/s Ponoka:	ND	0.2		ND				
d/s Camrose Ck:	ND	0.67		ND	ND		ND	ND/ND
Driedmeat Lake:		0.25						
Forestburg Res'r:		ND						
Hwy 872:	ND	0.26		ND				
Unwin:	ND	ND		ND		ND	ND	ND/ND
Battleford:	ND	ND		ND				

Name: Trifluralin (2,6-dinitro-N,N-dipropyl-4-(trifluoromethyl) benzenamine)
(Trade name: Treflan, Rival)
Group: Dinitroanalines
Uses: Control of wild oats and foxtail in barley, oilseed, and special crops (vegetables).
Toxicity: Very low acute mammalian toxicity. Acute oral LD50(rats)=5000-10000 mg/Kg. In clean water, fish are sensitive; in turbid waters, trifluralin binds to suspended sediment, increasing fish tolerance.
Alberta Usage: Large (>500,000 kg a.i./annum). Registered for Canadian use in 1962.
Application Period: Spring before weed emergence. June-Sept on summerfallow. September to freeze-up on legumes and oilseeds
Objectives or Guidelines: NYSDEC: 35 ug/L (MAC Drinking Water)
Detection Limits: Water (1.0 liter): 5 ng/L; (LSE): 0.4 ng/L
Sediment, Biota: 0.2 ng/G (89), 1 ng/G (90)

Summary of Results:

	1989						1990	
	May	June	July	Aug	Sep	Oct	Feb	Apr
A. WATER (results in ng/L)								
Hwy 611:	ND	IS	IS			ND	ND	ND
u/s Ponoka:	ND	ND	ND			ND	ND	
d/s Camrose Ck:	ND	IS	IS			ND	ND	ND
Hwy 872:	0.42	ND	ND			ND	ND	
Unwin:	ND	ND	ND			ND	ND	ND
Unwin (1 liter):	SD	ND	ND	ND	ND	ND	ND	ND
Battleford:	ND	ND	ND			ND	ND	
B. BOTTOM SEDIMENT (results in ng/G dry weight) (bolded results indicated suspended sediment)								
Battle Lake:		ND						
Hwy 611:	ND	ND		ND	ND		ND	ND/ND
u/s Ponoka:	ND	ND		ND				
d/s CamroseCk:	ND	ND		ND	ND		ND	ND/ND
Driedmeat Lake:		ND						
Forestburg Res'r:		ND						
Hwy 872:	ND	ND		ND				
Unwin:	ND	ND		ND		ND	ND	ND/ND
Battleford:	ND	ND		ND				

Name: Gamma BHC (Gamma HCH) (1,2,3,4,5,6 hexachlorocylohexane)
Trade name: Lindane
Group: Organochlorine Insecticide
Uses: Seed treatment for a variety of seed to control wireworms; less common uses include lice treatment on livestock and insect control in and around buildings.
Toxicity: High acute mammalian toxicity. Acute oral LD50(rats)=88-270 mg/Kg. Toxic to fish, birds, and other wildlife.
Alberta Usage: Moderate (100,000-500,000 kg a.i./annum)
Application Period: Spring and fall seeding.
Objectives or Guidelines: CCREM (1987): 0.01 ug/L (total isomers) (protection of aquatic life)
Detection Limits: Water (1.0 liter): 1 ng/L; (LSE): 0.4 ng/L
Sediment, Biota: 0.4 ng/G (89), 4 ng/G (90)

Summary of Results:

	1989						1990	
	May	June	July	Aug	Sep	Oct	Feb	Apr
A. WATER (results in ng/L)								
Hwy 611:	ND	ND	ND			ND	ND	0.14
u/s Ponoka:	ND	0.86	0.97			ND	0.63	
d/s CamroseCk:	ND	ND	ND			ND	ND	0.81
Hwy 872:	ND	1.10	ND			0.25	ND	
Unwin:	ND	ND	1.70			0.1	ND	3.27
Unwin (1 liter):	3.0	4.0	4.0	1.0	ND	ND	ND	3.0
Battleford:	ND	ND	0.60			ND	ND	
B. BOTTOM SEDIMENT (results in ng/G dry weight)								
Battle Lake:		ND						
Hwy 611:	ND	ND		ND	ND		ND	ND/ND
u/s Ponoka:	ND	ND		ND				
d/s Camrose Ck:	ND	ND		ND	ND		ND	ND/ND
Driedmeat Lake:		ND						
Forestburg Res'r:		ND						
Hwy 872:	ND	ND		ND				
Unwin:	ND	ND		ND		ND	ND	ND/ND
Battleford:	ND	ND		ND				

Name: Alpha BHC (Alpha HCH) (1,2,3,4,5,6 hexachlorocylohexane)
(alpha isomer of gamma BHC)
Group: Organochlorine Insecticide
Uses: see gamma BHC
Toxicity: Low acute mammalian toxicity. Chronic and cumulative.
Alberta Usage: Isomer of gamma BHC
Objectives or Guidelines: CCREM (1987): 0.01 ug/L (total isomers)
(protection of aquatic life)
Detection Limits: Water (1.0 liter): 1.0 ng/L; (LSE): 1.3 ng/L
Sediment, Biota: 0.4 ng/G (89), 4 ng/G (90)

Summary of Results:

	1989						1990	
	May	June	July	Aug	Sep	Oct	Feb	Apr
A. WATER (results in ng/L)								
Hwy 611:	ND	ND	ND			ND	ND * 0.5	
u/s Ponoka:	ND	ND	ND			ND	ND	
d/s CamroseCk:	ND	ND	ND			ND	ND * 0.63	
Hwy 872:	ND	ND	ND			ND	ND	
Unwin:	ND	ND	ND			ND	ND	1.97
Unwin (1 liter):	2.0	2.0	2.0	2.0	2.0	2.0	ND	1.0
Battleford:	ND	ND	ND			ND	ND	
B. BOTTOM SEDIMENT (results in ng/G dry weight)								
Battle Lake:		ND						
Hwy 611:	ND	ND		ND	ND		ND	ND/ND
u/s Ponoka:	ND	ND		ND				
d/s CamroseCk:	ND	ND		ND	ND		ND	ND/ND
Driedmeat Lake:		ND						
Forestburg Res'r:		ND						
Hwy 872:	ND	ND		ND				
Unwin:	ND	ND		ND		ND	ND	ND/ND
Battleford:	ND	ND		ND				

PESTICIDE CONCENTRATIONS IN AQUATIC INVERTEBRATES AND MACROPHYTES

Location: Battle River at Highway 611

Species Key: i1 (Amphipoda), i2 (Sphaeriidae), i3 (Simuliidae), i4 (Hirudinea), i5 (Tubificidae), i6 (Chironimadae), i7 (Unionidae), i8 (Gastropoda)

a1 (filamentous green algae)
m1 (Potamogeton richardsonii)

(Concentrations in ng/G wet weight)

	89/06/20			89/09/26				89/08/01	
	i1	i2	i3	i1	i2	i8	i4	a1	m1
Trifluralin	<.2	<.2	<.2	<1	<1	<1	<1	<1	<1
Diallate	<4.	<4.	<4.	<4	<4	<4	<4	<4	<4
Triallate	<.2	<.2	<.2	<2	<2	<2	<2	<2	<2
Atrazine	<15	<15	<15	<4	<4	7.0	<4	11.5	<4
Barban	<4.	<4.	<4.	<4	<4	<4	<4	<4	<4
Diclofop-Me	<1.5	<1.5	<1.5	<4	<4	<4	<4	<4	<4
Endaven	<1.	<1.	<1.	<2	<2	<2	<2	<2	<2
Metolachlor	<25	<25.	<25.	10.6	<4	8.9	<4	10.9	40.
HCB	<.2	<.2	<.2	<4	<4	<4	<4	<4	<4
a-BHC	<.4	<.4	<.4	<4	<4	<4	<4	<4	<4
g-BHC	<.4	<.4	<.4	<4	<4	<4	<4	<4	<4
Heptachlor	<.4	<.4	<.4	<4	<4	<4	<4	<4	<4
Aldrin	<.6	<.6	<.6	<4	<4	<4	<4	<4	<4
Hept Epoxide	<.1	<.1	<.1	<4	<4	<4	<4	<4	<4
g Chlordane	<.2	<.2	<.2	<4	<4	<4	<4	<4	<4
a Chlordane	<.2	<.2	<.2	<4	<4	<4	<4	<4	<4
a Endosulphan	<.15	<.15	<.15	<4	<4	<4	<4	<4	<4
pp-DDE	0.94	<.5	<.5	<4	<4	<4	<4	<4	<4
Dieldrin	<.2	<.2	<.2	<4	<4	<4	<4	<4	<4
Endrin	<.25	<.25	<.25	<4	<4	<4	<4	<4	<4
op-DDT	<.65	<.65	<.65	<4	<4	<4	<4	<4	<4
pp-TDE	<1.	<1.	<1.	<4	<4	<4	<4	<4	<4
pp-DDT	<1.25	<1.25	<1.25	<4	<4	<4	<4	<4	<4
b Endosulphan	<.65	<.65	<.65	<4	<4	<4	<4	<4	<4
Mirex	<.3	<.3	<.3	<4	<4	<4	<4	<4	<4
pp-Methoxyclor	<2.5	<2.5	<2.5	<4	<4	<4	<4	<4	<4
Total PCB	<25	<25	<25	<9	<9	<9	<9	<9	<9

Location: Battle River at Highway 53 (Upstream of Ponoka)

Species Key: i1 (Amphipoda), i2 (Sphaeriidae), i3 (Simuliidae), i4 (Hirudinea), i5 (Tubificidae), i6 (Chironimadae), i7 (Unionidae, i8 (Gastropoda)

a1 (filamentous green algae),
m1 (Potamogeton richardsonii)

(Concentrations in ng/G wet weight)

	89/06/21				
	i1	i2	i3	i4	17
Trifluralin	<.2	<.2	<.2	<.2	<.2
Diallate	<4.	<4.	<4.	<4.	<4.
Triallate	<.2	<.2	<.2	<.2	<.2
Atrazine	<15	<15	<15	<15	<15
Barban	<4.	<4.	<4.	<4.	<4.
Diclofop-Me	<1.5	<1.5	<1.5	<1.5	<1.5
Endaven	<1.	<1.	<1.	<1.	<1.
Metolachlor	<25	<25.	<25.	<25.	<25.
HCB	<.2	<.2	<.2	<.2	<.2
a-BHC	<.4	<.4	<.4	<.4	<.4
g-BHC	<.4	<.4	<.4	<.4	<.4
Heptachlor	<.4	<.4	<.4	<.4	<.4
Aldrin	<.6	<.6	<.6	<.6	<.6
Hept Epoxide	<.1	<.1	<.1	<.1	<.1
g Chlordane	<.2	<.2	<.2	<.2	<.2
a Chlordane	<.2	<.2	<.2	<.2	<.2
a Endosulphan	<.15	<.15	<.15	<.15	<.15
pp-DDE	<.5	<.5	<.5	<.5	<.5
Dieldrin	<.2	<.2	<.2	<.2	<.2
Endrin	<.25	<.25	<.25	<.25	<.25
op-DDT	<.65	<.65	<.65	<.65	<.65
pp-TDE	<1.	<1.	<1.	<1.	<1.
pp-DDT	<1.25	<1.25	<1.25	<1.25	<1.25
b Endosulphan	<.65	<.65	<.65	<.65	<.65
Mirex	<.3	<.3	<.3	<.3	<.3
pp-Methoxyclor	<2.5	<2.5	<2.5	<2.5	<2.5
Total PCB	<25	<25	<25	<25	<25

Location: Battle River downstream of Camrose Creek

Species Key: i1 (Amphipoda), i2 (Sphaeriidae), i3 (Simuliidae), i4 (Hirudinea), i5 (Tubificidae), i6 (Chironimadae), i7 (Unionidae), i8 (Gastropoda)

a1 (filamentous green algae), m1 (Potamogeton richardsonii)

(Concentrations in ng/G wet weight)

	89/06/22				89/09/28				89/08/02	
	i1	i4	i5	i6	i1	i4	i5	i8	a1	m1
Trifluralin	<.2	<.2	<.2	<.2	<1	<1	<1	<1	<1	<1
Diallate	<4.	<4.	<4.	<4.	<4	<4	<4	<4	<4	<4
Triallate	<.2	<.2	<.2	<.2	<2	5.3	23.2	<2	<2	<2
Atrazine	<15	<15	<15	<15	<4	<4	<4	<4	<4	<4
Barban	<4.	<4.	<4.	<4.	<4	<4	<4	<4	<4	<4
Diclofop-Me	<1.5	<1.5	<1.5	<1.5	<4	<4	<4	<4	<4	<4
Endaven	<1.	<1.	<1.	<1.	<2	<2	<2	<2	<2	<2
Metolachlor	<25	<25.	<25.	<25.	4.3	<4	<4	8.2	<4	<4
HCB	<.2	<.2	<.2	<.2	<4	<4	<4	<4	<4	<4
a-BHC	<.4	<.4	<.4	<.4	<4	<4	<4	<4	<4	<4
g-BHC	<.4	<.4	<.4	<.4	<4	<4	<4	<4	<4	<4
Heptachlor	<.4	<.4	<.4	<.4	<4	<4	<4	<4	<4	<4
Aldrin	<.6	<.6	<.6	<.6	<4	<4	<4	<4	<4	<4
Hept Epoxide	<.1	<.1	<.1	<.1	<4	<4	<4	<4	<4	<4
a Chlordane	<.2	<.2	<.2	<.2	<4	<4	<4	<4	<4	<4
g Chlordane	<.2	<.2	<.2	<.2	<4	<4	<4	<4	<4	<4
a Endosulphan	<.15	<.15	<.15	<.15	<4	<4	<4	<4	<4	<4
pp-DDE	<.5	<.5	<.5	<.5	<4	<4	<4	<4	<4	<4
Dieldrin	<.2	<.2	<.2	<.2	<4	<4	<4	<4	<4	<4
Endrin	<.25	<.25	<.25	<.25	<4	<4	<4	<4	<4	<4
op-DDT	<.65	<.65	<.65	<.65	<4	<4	<4	<4	<4	<4
pp-TDE	<1.	<1.	<1.	<1.	<4	<4	<4	<4	<4	<4
pp-DDT	<1.25	<1.25	<1.25	<1.25	<4	<4	<4	<4	<4	<4
b Endosulphan	<.65	<.65	<.65	<.65	<4	<4	<4	<4	<4	<4
Mirex	<.3	<.3	<.3	<.3	<4	<4	<4	<4	<4	<4
pp-Methoxyclor	<2.5	<2.5	<2.5	<2.5	<4	<4	<4	<4	<4	<4
Total PCB	<25	<25	<25	<25	<9	<9	<9	<9	<9	<9

Location: Battle River at Highway 872

Species Key: i1 (Amphipoda), i2 (Sphaeriidae), i3 (Simuliidae), i4 (Hirudinea), i5 (Tubificidae), i6 (Chironimadae), i7 (Unionidae), i8 (Gastropoda),

a1 (filamentous green algae),
m1 (Potamogeton richardsonii)

(Concentrations in ng/G wet weight)

	89/06/23				89/09/29
	i1	i4	i7	i2	i4
Trifluralin	<.2	<.2	<.2	<.2	<1
Diallate	<4.	<4.	<4.	<4.	<4
Triallate	<.2	<.2	<.2	<.2	<2
Atrazine	<15	<15	<15	<15	<4
Barban	<4.	<4.	<4.	<4.	<4
Diclofop-Me	<1.5	<1.5	<1.5	<1.5	<4
Endaven	<1.	<1.	<1.	<1.	<2
Metolachlor	<25	<25.	<25.	<25.	<4
HCB	<.2	<.2	<.2	<.2	<4
a-BHC	<.4	<.4	<.4	<.4	<4
g-BHC	<.4	<.4	<.4	<.4	<4
Heptachlor	<.4	<.4	<.4	<.4	<4
Aldrin	<.6	<.6	<.6	<.6	<4
Hept Epoxide	<.1	<.1	<.1	<.1	<4
g Chlordane	<.2	<.2	<.2	<.2	<4
a Chlordane	<.2	<.2	<.2	<.2	<4
a Endosulphan	<.15	<.15	<.15	<.15	<4
pp-DDE	<.5	<.5	<.5	<.5	<4
Dieldrin	<.2	<.2	<.2	<.2	<4
Endrin	<.25	<.25	<.25	<.25	<4
op-DDT	<.65	<.65	<.65	<.65	<4
pp-TDE	<1.	<1.	<1.	<1.	<4
pp-DDT	<1.25	<1.25	<1.25	<1.25	<4
b Endosulphan	<.65	<.65	<.65	<.65	<4
Mirex	<.3	<.3	<.3	<.3	<4
pp-Methoxyclor	<2.5	<2.5	<2.5	<2.5	<4
Total PCB	<25	<25	<25	<25	<9

Location: Battle River near Unwin

Species Key: i1 (Amphipoda), i2 (Sphaeriidae), i3 (Simuliidae), i4 (Hirudinea), i5 (Tubificidae), i6 (Chironimadae), i7 (Unionidae), i8 (Gastropoda)

a1 (filamentous green algae), m1 (Potamogeton richardsoni

(Concentrations in ng/G wet weight)

	89/06/28		89/10/03				89/08/03	
	i1	i2	i1	i2	i7	i7	a1	m1
Trifluralin	<.2	<.2	<1	<1	<1	<1	<1	<1
Diallate	<4.	<4.	<4	<4	<4	<4	<4	<4
Triallate	<.2	<.2	<2	<2	<2	3.9	<2	<2
Atrazine	<15	<15	<4	<4	<4	<4	<4	<4
Barban	<4.	<4.	<4	<4	<4	<4	<4	<4
Diclofop-Me	<1.5	<1.5	<4	<4	<4	<4	<4	<4
Endaven	<1.	<1.	<2	<2	<2	<2	<2	<2
Metolachlor	<25	<25.	4.1	<4	<4	<4	<4	<4
HCB	<.2	<.2	<4	<4	<4	<4	<4	<4
a-BHC	<.4	<.4	<4	<4	<4	<4	<4	<4
g-BHC	<.4	<.4	<4	<4	<4	<4	<4	<4
Heptachlor	<.4	<.4	<4	<4	<4	<4	<4	<4
Aldrin	<.6	<.6	<4	<4	<4	<4	<4	<4
Hept Epoxide	<.1	<.1	<4	<4	<4	<4	<4	<4
g Chlordane	<.2	<.2	<4	<4	<4	<4	<4	<4
a Chlordane	<.2	<.2	<4	<4	<4	<4	<4	<4
a Endosulphan	<.15	<.15	<4	<4	<4	<4	<4	<4
pp-DDE	<.5	<.5	<4	<4	<4	<4	<4	<4
Dieldrin	<.2	<.2	<4	<4	<4	<4	<4	4.0
Endrin	<.25	<.25	<4	<4	<4	<4	<4	<4
op-DDT	<.65	<.65	<4	<4	<4	<4	<4	<4
pp-TDE	<1.	<1.	<4	<4	<4	<4	<4	<4
pp-DDT	<1.25	<1.25	<4	<4	<4	<4	<4	<4
b Endosulphan	<.65	<.65	<4	<4	<4	<4	<4	<4
Mirex	<.3	<.3	<4	<4	<4	<4	<4	<4
pp-Methoxyclor	<2.5	<2.5	<4	<4	<4	<4	<4	<4
Total PCB	<25	<25	<9	<9	<9	<9	<9	<9

Location: Battle River near Battleford

Species Key: i1 (Amphipoda), i2 (Sphaeriidae), i3 (Simuliidae), i4 (Hirudinea), i5 (Tubificidae), i6 (Chironimadae), i7 (Unionidae), i8 (Gastropoda

a1 (filamentous green algae),
m1 (Potamogeton richardsonii)

(Concentrations in ng/G wet weight)

	89/06/29		
	i1	i2	i7
Trifluralin	<.2	<.2	<.2
Triallate	<4.	<4.	<4.
Triallate	<.2	<.2	<.2
Atrazine	<15	<15	<15
Barban	<4.	<4.	<4.
Diclofop-Me	<1.5	<1.5	<1.5
Endaven	<1.	<1.	<1.
Metolachlor	<25	<25.	<25.
HCB	<.2	<.2	<.2
a-BHC	<.4	<.4	<.4
g-BHC	<.4	<.4	<.4
Heptachlor	<.4	<.4	<.4
Aldrin	<.6	<.6	<.6
Hept Epoxide	<.1	<.1	<.1
Chlordane	<.2	<.2	<.2
a Chlordane	<.2	<.2	<.2
a Endosulphan	<.15	<.15	<.15
pp-DDE	<.5	<.5	<.5
Dieldrin	<.2	<.2	<.2
Endrin	<.25	<.25	<.25
op-DDT	<.65	<.65	<.65
pp-TDE	<1.	<1.	<1.
pp-DDT	<1.25	<1.25	<1.25
b Endosulphan	<.65	<.65	<.65
Mirex	<.3	<.3	<.3
pp-Methoxyclor	<2.5	<2.5	<2.5
Total PCB	<25	<25	<25

PESTICIDE CONCENTRATIONS IN FISH:

Location: Forestburg Reservoir above Alberta Power Station

Species Key: pm (pike muscle no skin), pl (pike liver),
sm (white sucker muscle no skin)
sl (white sucker liver)

(Concentrations in ng/G wet weight)

	1989/11/01				1990/04/26					
	pm	pl	sm	sl	pl1	pl2	pl3	pl4	sl1	sl2
Trifluralin	<.2	<.2	<.2	<.2	1.0	<1	<1	<1	<1	<1
Diallate	<4.	<4.	<4.	<4.	<4	<4	<4	<4	<4	<4
Triallate	<.2	<.2	<.2	<.2	31.8	<2	<2	<2	<2	<2
Atrazine	<15	<15	<15	<15	<4	<4	<4	<4	<4	<4
Barban	<4.	<4.	<4.	<4.	<4	<4	<4	<4	<4	<4
Diclofop-Me	<1.5	<1.5	<1.5	<1.5	<4	<4	<4	<4	<4	<4
Endaven	<1.	<1.	<1.	<1.	<2	<2	<2	<2	<2	<2
Metolachlor	<25	<25.	<25.	<25.	4.5	<4	4.6	<4	<4	<4
HCB	<.2	2.8	<.2	<.2	<4	<4	<4	<4	<4	<4
a-BHC	<.4	<.4	<.4	<.4	<4	<4	<4	<4	<4	<4
g-BHC	<.4	<.4	<.4	<.4	<4	<4	<4	<4	<4	<4
Heptachlor	<.4	<.4	<.4	<.4	<4	<4	<4	<4	<4	<4
Aldrin	<.6	<.6	<.6	<.6	<4	<4	<4	<4	<4	<4
Hept Epoxide	<.1	<.1	<.1	<.1	<4	<4	<4	<4	<4	<4
g Chlordane	<.2	<.2	<.2	<.2	<4	<4	<4	<4	<4	<4
a Chlordane	<.2	<.2	<.2	<.2	<4	<4	<4	<4	<4	<4
a Endosulphan	<.15	<.15	<.15	<.15	<4	<4	<4	<4	<4	<4
pp-DDE	<.5	<.5	<.5	<.5	<4	<4	<4	<4	<4	<4
Dieldrin	<.2	<.2	<.2	<.2	<4	<4	<4	<4	<4	<4
Endrin	<.25	<.25	<.25	<.25	<4	<4	<4	<4	<4	<4
op-DDT	<.65	<.65	<.65	<.65	<4	<4	<4	<4	<4	<4
pp-TDE	<1.	<1.	<1.	<1.	<4	<4	<4	<4	<4	<4
pp-DDT	<1.25	<1.25	<1.25	<1.25	<4	<4	<4	<4	<4	<4
b Endosulphan	<.65	<.65	<.65	<.65	<4	<4	<4	<4	<4	<4
Mirex	<.3	<.3	<.3	<.3	<4	<4	<4	<4	<4	<4
pp-Methoxyclor	<2.5	<2.5	<2.5	<2.5	<4	<4	<4	<4	<4	<4
Total PCB	<25	246.9	<25	34.2	<9	<9	<9	<9	<9	<9