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NUTRIENT AND CONTAMINANT PATHWAYS IN THE BOW AND OLDMAN RIVERS, ALBERTA
1980-1981

FINAL REPORT
to
ENVIRONMENT CANADA
CONTRACT OSU80-00056
MARCH 31, 1982

by

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EXECUTIVE SUMMARY

The Bow and Oldman Rivers with their tributaries, together with the Red Deer, are the principal river systems of Southern Alberta. The Bow and Oldman merge to form the South Saskatchewan River in south-central Alberta. The South Saskatchewan River system traverses a variety of climatic regimes.The basin hydrography is shaped by the alpine sources of the Bow and Oldman Rivers and, in particular, by various glacial sources of the Bow.

The Bow and Oldman each have one major urban point source -- Calgary and Lethbridge respectively. The effects of diffuse sources are not well known upon major rivers in this region. Large scale irrigation in Alberta is one potential diffuse source of sediments, nutrients, heavy metals and agricultural chemicals. Some of these are addressed in this study.

Over the past decade public perception of water quality of the Bow River has been influenced by the dense growths of rooted macrophytes which thrive below the Calgry sewage outfalls and which in 1979 extended downstream to the confluence of the Bow and Oldman Rivers. These form nuisance rafts of organic debris which clog water intakes as far downstream as Medicine Hat. The role of aquatic weeds in uptake and storage of phosphorus and contaminants is addressed here.

This study focusses primarily on the reach of river extending downstream from Calgary on the Bow, and from Lethbridge on the Oldman to their confluence at `Grand Forks´ (Bow Island), a river distance of 339 km and 177 km respectively. Each reach commences with a major point source, then flows for long distances across increasingly arid conditions where potential anthropogenic impact is restricted to water diversion for irrigation purposes, irrigation return-flows and the occasional riparian feedlot.

Water and suspended sediment samples were collected at thirteen sites (eight on the Bow and five on the Oldman) during the early summer(´80), summer(´80), fall(´80) and spring (´81) discharge regimes. Samples were collected systematically downstream to reflect time-of-travel (hydrologic synoptic sampling). Aquatic plants were collected during the summer and fall of 1980. A selection of irrigation return flows was sampled every two to three weeks for much of the irrigation season (June to Sept., 1980).

The major scientific findings and management implications are summarized below. `S´ denotes scientific finding; `M´ denotes management implication. Unless otherwise noted, `sediment´ refers to suspended sediment.

SUSPENDED SEDIMENT

S1. During periods of high water with large concentrations of suspended sediment, suspended matter dominates the chemistry of phosphorus and heavy metals in water samples

S2. "Total" phosphorus and heavy metals in water samples during high water are much larger than concentrations at other times of the year reflecting the abundance of suspended sediment.

S3. During high water periods, sediment chemistry is largely at background reflecting diffuse sources of sediment from eroding prairie and foothill surfaces.

S4. For most substances the sediment fraction is responsible for the bulk of the chemical load transported over the sampled six month period (May - October). Much of this load is not, however, bioavailable within a riverine context but may have impact on downstream sedimentary environments (reservoirs).

S5. Particle size and organic content exhibit distinct differences at different times of the year.

1M. Bottom sediments, because of their coarse nature, are not thought to be important sinks or sources of nutrient or contaminants in these rivers. These sediments act as a rooting environment and, due to their coarse nature, permit easy passage of nutrient-rich river water into the rooting zone.

PHOSPHORUS

S1. During high water in spring and early summer, TP in water is comprised almost entirely of sediment-associated phosphorus in the Oldman River. This holds for the Bow in spring; hoever, the major phosphorus input at Calgary is manifested in larger amounts of TDP during the balance of the year.

S2. Downstream increases in Total-P in water during spring high flow reflect substantial inputs of suspended matter from tributaries and bank collapse.

S3. There is a substantial increase in TP below each urban area, then a progressive loss downstream during low water periods.

S4. During low flow (summer and fall) there is a major increase in TDP immediately below urban areas in each river, with a progressive loss of TDP and gain in particulate-associated P over the remaining length of river channel. This suggests conversion of dissolved-P to sediment-associated forms through a combination of biological and geochemical processes.

S5. Apatite-P dominates the sediment-associated phosphorus fraction in spring and early summer (high flow). The nonapatite and organic phosphorus fractions become large in summer and fall.

M1. Conventional measures of TP and TDP in water adequately characterize amounts, spatial and temporal patterns of phosphorus, and conversion to particulate-associated phosphorus. These measures do not account for the very large phosphorus loads accumulated in biomass and which are transported downstream following senescence of the macrophyte population.

M2. Any measure of phosphorus during high flow is essentially a measure of diffuse sources of phosphorus flux originating from eroding soil surfaces.

M3. Sediment-associated phosphorus forms of NAI-P and O-P are not biologically important in either river, mainly because of the absence of a major sink environment in Alberta. It is not known to what extent either fraction may become available in sink locations further downstream.

M4. For downstream management purposes sediment-associated phosphorus species should be characterized for the different hydrologic seasons in order to estimate the loadings of potentially available phosphorus forms (NAI-P & O-P). For management purposes this needs to be determined only a few times per year using several replicate samples. Although significant variance may be expected, it is commensurate with those errors inherent in loadings calculations which are introduced by the many assumptions used in loadings algorithms.

M5. Bottom sediments, because of their coarse nature, are not considered to be a significant sink or source of phosphorus.

M6. Organic-P levels in plants in the Bow and Oldman Rivers are not useful indicators of nutrient stress because of equivalent luxury uptake under a variety of different nutrient conditions. Alternatively, plant density and size are related to nutrient conditions. This relationship is complicated by the effect of downstream seeding (increased productivity) and plant elimination by hydraulic forces during periods of high flow.

M7. Plants appear to be able to survive periods of nutrient deficiency because of the ability to quickly assimilate phosphorus (luxury uptake) during nutrient-rich periods. The frequency, timing and concentration of uncontrolled sewage discharge should be examined in reference to plant physiology to define in operational terms the degree to which such discharges may become counter-productive to phosphorus abatement programs.

M8. Irrigation return flows are marginal contributors to TDP in terms of prevailing levels of TDP in receiving rivers. Whether return flows will assume greater significance if urban point sources are dramatically reduced would require further study.

M9. Sediment-associated phosphorus from irrigation return flows is not a contributor to enrichment in either river.

Heavy Metals

S1. Most filterable and many total metal determinations in water are below conventional detection limits. Levels in spring are up to ten-fold higher than at other times of the year, reflecting large amounts of suspended sediment in the water sample.

S2. Total metals in water in spring increase downstream, reflecting tributary inputs of suspended sediment.

S3. Sediment-related metals illustrate pronounced seasonal differences.

S4. Sediment-related metals in spring tend to be at background (unenriched) levels reflecting diffuse sources of sediment and have little downstream trend.

S5. All metals are detectable on suspended matter and, with the exception of cobalt, in macrophytes and filamentous algae.

S6. Sediment-related metals in summer and fall are generally higher in the Bow than in the Oldman River.

S7. The chemistry of suspended sediment and plants in summer and fall illustrate distinct downstream trends for many metals.

S8. The six-month loading (May-Oct.) of most metals is dominated by the spring load associated with suspended sediment transport. This load is not considered to be bioavailable in these rivers.

S9. With the single exception of iron, biomass storage of heavy metals in the Bow River greatly exceeds the six-month load of each metal as calculated from water chemistry. This is especially so for the trace metals.

S10. A number of metals peak at Taber on the Oldman River, indicating the presence of an unidentified source between Coaldale and Taber. These observations are made upstream of any discharge originating from the sugar processing plant in Taber.

S11. Metal species associated with suspended sediments in irrigation-return flows are largely unavailable.

M1. The inability to measure many metals as `filterable´ and some as `total´ using conventional flame AA precludes conventional measurements for determining heavy metals in time and space.

M2. The inability to detect most metals in filterable form precludes any assessment of bioavailability of metals using conventional chemical measures.

M3. All metals are detectable on suspended sediment and, with the exception of cobalt, in filamentous algae and rooted macrophytes in both rivers.

M4. Suspended sediment and plants reflect downstream changes in river chemistry and demarcate zones of metal stress where conventional water chemistry indicate no significant change (e.g. Zn, Cu, Mn).

M5. Macrophytes and filamentous algae are responsive to ambient metal levels in water. They are, therefore, useful indicators of metal stress in rivers. Plant assay is a useful alternative to conventional water chemistry both for determining presence/absence of a metal and for estimating the bioavailable component of the `total´ metal flux.

M6. Water, sediment and plant data indicate a metal source immediately upstream from Taber.

M7. There appears to be chronic, low level leakage of metals from sediments in Bassano Dam reservoir. The impact is generally lost by Bow City. Effect of metal transport to Lake Newell is not known.

M8. Irrigation-return flows do not contribute available metals to the Bow and Oldman Rivers. Speciation chemistry and comparative data from prairie soils indicates that suspended sediment metal chemistry is typical of unenriched prairie soils.

M9. Loadings of metals as calculated from conventional chemical measures are grossly inaccurate regardless of the frequency of observation due to metal storage in biomass.

Organochlorine Residues

S1. Of a suite of chlorobenzene isomers, nonionic pesticides, PCB and mirex, only 135, 124, 123 chlorobenzenes, α, β-HCH, α chlordane, dieldrin, DDT and its metabolites and PCB are detectable. These are all generally at or near detection in all seasons.

S2. Detectable chlorbenzenes and other OC residues are preferentially associated with one or more of the plant, suspended sediment or water phases. These associations are consistent from season to season. Many of the less soluble residues cannot be detected in bulk water samples but can be detected in sediment and/or plant samples.

M1. Unlike most soluble chlorobenzene isomers, other OC residues are generally not detectable in bulk water samples but can be routinely found in suspended sediment and/or plant samples. This implies that suspended sediment and plant matter are useful monitoring media for those substances which are largely insoluble and which are difficult to detect in bulk water samples.

M2. Plants can be used in a semi-quantitative manner to determine the chemical forms which are bioavailable in a riverine context. Accumulation of these substances in rivers having significant biomass could constitute an important and unmeasured load which is deliverable downstream following plant senescence.

M3. Organochlorine residues associated with suspended sediment are probably not significant in a riverine context but do constitute a measurable load delivered downstream. These contaminants may become biologically significant once the sediments are deposited in a sink environment.

NUTRIENT AND CONTAMINANT PATHWAYS IN THE BOW AND OLDMAN RIVERS, ALBERTA

INTRODUCTION

The Bow and Oldman Rivers with their tributaries, together with the Red Deer, are the principal river systems of Southern Alberta. The Bow and the Oldman merge to form the South Saskatchewan River in south-central Alberta (Figure 1). The North and South Saskatchewan Rivers are the two major interprovincial rivers of western Canada which rise in the western cordillera of Alberta and flow eastwards, merging in the province of Saskatchewan and flowing eventually to Hudson Bay via Manitoba.

The South Saskatchewan River system traverses a variety of climatic regimes. The basic hydrography is shaped, however, by the alpine sources of the Bow and Oldman Rivers and, in particular, by various glacial sources of the Bow. Both rivers flow from the mountains through increasingly arid landscapes as they traverse the Palliser triangle of southeastern Alberta where they merge to form the main stem of the South Saskatchewan River. Although the dry plains climate does not directly impact upon river hydrology, it has an important indirect impact insofar as the large irrigation areas of southeastern Alberta require large extractions of river water at Carseland and Bassano on the Bow, and Brocket on the Oldman River.

The Bow and Oldman each have one major urban point source -

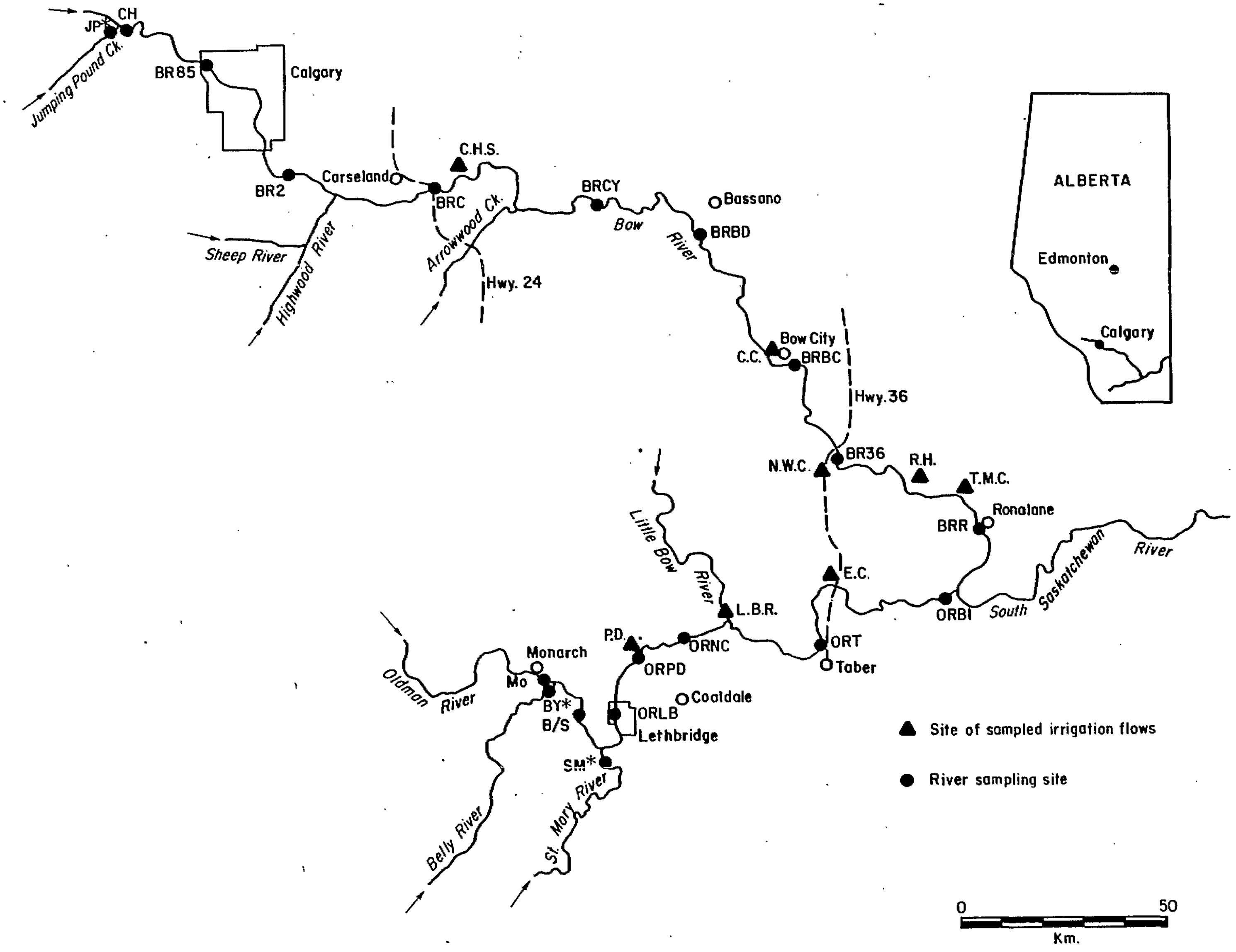


Figure 1. River and Irrigation Return Flow Sites on the Bow and Oldman Rivers, Southern Alberta.

Calgary and Lethbridge respectively. The effects of diffuse sources are not well known upon major rivers in this region. Large scale irrigation in Alberta is one potentially significant diffuse source of nutrients, heavy metals and organic contaminants; therefore, the examination of selected irrigation return flows is included in this study. An indirect impact of irrigation upon river water quality is the severe reduction of river flow during periods of substantial water extraction with attendant problems of periodic deoxygenation etc., in summer months.

The unpredictable character of rainfall and snow accumulation and melt in the plains region make the assessment of non-irrigated agricultural impacts on river water quality difficult to assess. In this study, we were able to sample in spring of 1980 and 1981 at times of significant regional rain which had visible surface runoff over much of the Western Plains and foothills area. The extent to which this is typical is difficult to ascertain. The major visual effect of surface runoff is the large suspended sediment loads transported by the Bow and Oldman Rivers and their various tributaries. Except under conditions of exceptional regional rain which necessarily produces surface erosion, sediment supply to these rivers downstream of the foothills appears to be dominated by periodic collapse of unconsolidated clay-rich bedrock into which the middle and lower course of both rivers are deeply entrenched. This observation is significant in that it may explain why certain metals levels on suspended sediment are attenuated in a downstream direction.

Both the Bow and Oldman River valleys served as glacial spillways during the late Pleistocene. Their bottom sediments are derived from glacial debris and are generally very coarse, comprised of gravel, cobbles and boulders. From a water quality perspective, the coarse nature of the bottom sediments is significant in that the absence of significant quantities of fine-grained material precludes any major sink or source for nutrients and contaminants in bottom materials. Although fine-grained suspended sediment may be lodged into bottom sediments as a result of hydraulic gradients within the bed, suspended sediment may be assumed to be transported down these rivers as a function of current velocity. Within the study region there are no significant settling environments. Carseland Dam is, in reality, a large weir without significant storage, and Bassano Dam, built in the early 1900's, has been completely silted in for many years.

Over the past decade public perception of water quality of the Bow River in particular has been influenced by the dense growths of rooted macophytes which thrive below the Calgary sewage outfalls and form nuisance rafts of organic debris which clog water intakes as far downstream as Medicine Hat. In September of 1979 macrophyte populations literally choked the Bow River as far downstream as Ronalane (immediately upstream of its confluence with the Oldman River, Figure 1), some 310 km from Calgary. In contrast, the Oldman River supports a generally sparse population of filamentous algae except in the reach immediately downstream from Lethbridge (Piyami Drain vicinity, Figure 1) where the growth occurs in nuisance quantities.

Significantly, a large June discharge in 1980 (Figures 2-4) which coincided with the first sampling trip of this research program, completely destroyed the Bow macrophyte community downstream from Bassano and significantly reduced the population in the reach from Calgary to Bassano. It is probable that bottom sediments were sufficiently mobilized to disturb the rooting environment. Macrophyte growth was not re-established by October 1980. High spring discharges in May of 1981 obscured any determination of macrophyte growth at the time of the last sampling run. Subsequent discussion with scientists from Alberta Environment indicate that the macrophyte population was sparse below Bassano Dam during the 1981 field year. It would appear, therefore, that hydrologic factors must be a major consideration in developing macrophyte control strategies on the Bow River.

This study focusses primarily on the reach of river extending downstream from Calgary on the Bow and from Lethbridge on the Oldman, to their confluence at 'Grand Forks'(Bow Island), a river distance of 339 km and 177 km respectively (Figure 1, Tables 1 & 2). Each reach commences with a major urban point source, thence traverses long distances across increasingly arid conditions where potential anthropogenic impact is restricted to irrigation return flows and, possibly, the occasional riparian feedlot. Compared with Eastern Canada the downstream transport of nutrients and contaminants is

TABLE 1: Sampling sites : 1980-81

Bow River	Field Code
1. Above Calgary: 85th St.Bridge	BR85
2. Downstream of Calgary STP's (Steer's Ranch)	BR2
3. Below Carseland Weir at Highway 24	BRC
4. Bow River near Cluny at Highway 842	BRCY
5. Bow River below Bassano Dam	BRBD
6. Bow River at Bow City (Highway 539)	BRBC
7. Bow River at Highway 36	BR36
8. Bow River at Ronalane Wasteway	BRR
Oldman River	
1. At Lethbridge; Highway 3	ORLB
2. Below Lethbridge near Piyami Drain	ORPD
3. Highway 845 near Coaldale	ORNC
4. Highway 864 near Taber	ORT
5. Upstream of South Saskatchewan R. at Grand Forks	ORBI
Auxiliary River Sites: Oldman River	
1. Oldman River below Monarch (downstream of Hwy 3)	MO*
2. Belly River above confluence	BY*
3. Oldman River between Belly & St. Mary River	B/S
4. St.Mary River above confluence	SM*
5. Oldman River below St.Mary River	ORLB'

* sample at mouth of tributary to Oldman River

Irrigation Return Flows	
(Oldman River)	
1. Piyami Drain; south of Picture Butte	P.D.
2. Little Bow River; east of Picture Butte	L.B.R.
3. Expanse Coulee; south of Vauxhall, at Highway 36	E.C.
(Bow River)	
4. New West Coulee; north of Vauxhall, at Highway 36	N.W.C.
5. Rolling Hills, Canal #1 (distribution canal) south of Rolling Hills	R.H.
6. Twelve Mile Coulee; southeast of Rolling Hills	T.M.C.
7. Coal Creek; at Bow City	C.C.
8. Cairn Hill Spillway; at Strangmuir, north of Carseland	C.H.S.

relatively uncomplicated by a multiplicity of competing land uses, large rural populations, high cattle densities, and closely-spaced municipal and industrial point sources common to eastern rivers. Indeed, with the exception of the Highwood River between Calgary and Carseland Dam and Arrowwood Creek between Carseland and Cluny (Figure 1) on the Bow, and the Little Bow flowing into the Oldman River, there are no major tributaries to either river throughout most of their studied length.

TABLE 2: Distances between river sampling sites (km)

	Distance	Cumulative Distance
Bow River		
BR85	0	0
BR2	43.1	43.1
BRC	40.0	83.1
BRCY	72.5	155.6
BRBD	38.8	194.4
BRBC	56.3	250.7
BR36	31.3	282.0
BRR	56.9	338.9
Oldman River		
MO	0	0
BY*	8.1	8.1
SM*	12.5	20.6
ORLB	15.0	35.6
ORPD	23.8	59.4
ORNC	18.1	77.5
ORT	38.8	116.3
ORBI	60.6	176.9

* Confluence with Oldman River.

These rivers, therefore, offer a relatively unique opportunity to examine in a relatively uncomplicated situation, the biogeochemical pathways of nutrients and contaminants over long distances under a range of seasonal discharge conditions. In this study, we are principally concerned with establishing the downstream and seasonal patterns of distributions of individual nutrient and contaminant forms amongst solution, suspended sediment (mineral and organic) and aquatic plants. The question of bioavailability is raised together with the general issue of transient in-stream storage by luxury uptake in aquatic weeds. In turn, this information permits an assessment of the value of conventional monitoring data to (i) characterize the chemical "state" of the river, (ii) identify spatial and temporal patterns of nutrient and toxic stress and, (iii) identify linkages between source of nutrient and contaminant inputs and their downsteam effects in order to predicting causality and to identify remedial options.

The intention was to establish geochemical patterns characteristic of each discharge regime. With only one sampling run per season, it is not possible to establish whether the results are "representative" of the particular regime in question. The question of representivity is not especially relevant in this study, however, as the objective was to establish major differences between seasons not minor variations within seasons.

Extended discussion of trends, analytical procedures, statistical analyses, etc., are found in M.Sc. theses of D.Blachford and H.Macdonald (in preparation).

A complicating effect of unkown proportions, especially in the Oldman River basin, is the effect of ash rain following the eruptions of Mt. St.Helens in Washington State in May and again in July of 1980. Indeed, one sampling run in July was abandonned after ash fell in the southern part of the Oldman basin following the July 22 eruption.

OBJECTIVES

For the Bow and Oldman Rivers:

1. Identify biogeochemical pathways of phosphorus, heavy metals and organochlorine compounds amongst water, plants and suspended sediments,
2. Define pathway characteristics in terms of discharge regimes which are typical of prairie rivers,
3. Define pathway characteristics taking into account time-of-travel, seasonality of point and diffuse sources, and potential riverine sinks,
4. Define spatial and seasonal resolution of element variance and covariance, and of geochemical and physical relationships with organic/inorganic matter, clay mineralogy*, particle-size distributions etc. and their relationships to Total and Filterable chemical forms,
5. Evaluate pathway information in the context of efficiency of conventional monitoring information to identify patterns and causality of nutrient and contaminant stress in the aquatic ecosystem.

* Clay mineralogy data are unavailable due to the small amounts of suspended material available in summer and fall sampling runs.

SAMPLING AND ANALYTICAL DESIGN

Site Selection and Sampling Strategy

Selection of river sampling sites involved consideration of point and diffuse sources, potential riverine sinks and accessibility. Because the program focussed upon the the influence of wastewater discharges from Calgary and Lethbridge on the Bow and Oldman Rivers respectively, a baseline site was chosen on each river immediately upstream of any potential urban impact (BR85 & ORLB; Figure 1,Table 1). Downstream sites (Primary sites,Figure 1) were chosen at approximately equidistant intervals (given appropriate road access) to permit spatial assessment of the downstream trends of biogeochemical cycling amongst water, aquatic plants and suspended matter (Table 2).

Major sources to the Bow River below Calgary are the Highwood River and Arrowwood Creek (Figure 1); in addition, there are a number of irrigation return flows and riparian feedlot operations. Major inputs to the Oldman river are the St.Mary and Belly Rivers immediately upstream from Lethbridge, and the Little Bow River below Lethbridge. A number of irrigation return flows enter the Oldman River, including substantial irrigation return flow water in the Little Bow River. An intermittent point source to the Oldman is the Taber sugar processing plant. As indicated by our data below, there appears to be some other significant but unidentified input to the Oldman upstream from Taber.

Auxiliary sampling sites (Figure 1) were added to the June 1980 run of the Oldman River in order to characterize the physical and geochemical nature of sediments and water for the Belly and St.Mary Rivers and their combined effect on the Oldman at a time when these rivers contribute major sediment loadings to the Oldman River system. Additional sites were added to the spring 1981 run on the Bow River to obtain a secondary baseline site for the Bow (CH) and to characterize the geochemical contribution from Jumping Pound Creek (JP) at a time when it was a major contributor of suspended sediment to the Bow upstream from Calgary.

Seven irrigation return flows and one irrigation distribution canal were sampled in 1980 (Figures 1 & 25) to represent major irrigation returns to the Bow and Oldman Rivers. The return flows characterize a variety of drainage areas, irrigation and cropping practices; together, the sampled flows drain an estimated 15% of the total irrigated land in Alberta.

The effects of seasonality upon chemical characteristics of solutes, solids and aquatic plants were evaluated by sampling during pronounced seasonal discharge regimes typical of prairie rivers. Figures 2-5 illustrate the positions on the annual hydrographs during which samples were obtained. The long-term record of each river is illustrated in Figure 6. Sampling was carried out in early summer (June), summer (Aug-Sept) and fall (Oct) of 1980, and early spring (May) of 1981. The early summer run in June of 1980 was a time of unseasonally high flow and sediment transport due to substantial regional rainfall superimposed on the discharge effects of alpine snowpack melt. Sampling in spring of 1981 coincided with peak flows due to foothill snowpack melt and substantial rainfall across southern Alberta.

The river sites were sampled sequentially downstream, representing the closest approximation to time-of-travel (hydrologic synoptic sampling) possible with the sampling equipment employed (Table 3). Elevated suspended sediment concentrations during spring and early summer runs allows sampling of up to two sites per day. Very low sediment concentrations in summer and fall required a full day per site to collect minimum quantities of suspended material. Suspended sediment data for each of the primary sites represent a time-integration of from 0.3 hr in spring/81 to >6 hr for summer and fall/80. The variation in sampling time reflects in-stream concentrations of suspended sediment. Data for the early summer (June) run of 1980 for sites MO, B/S, LB (Figure 1) represent spatially integrated samples collected whilst floating downstream at time-of-travel. These latter samples were obtained below the point of mixing of tributary inputs.

Water and suspended sediment samples were collected at each of

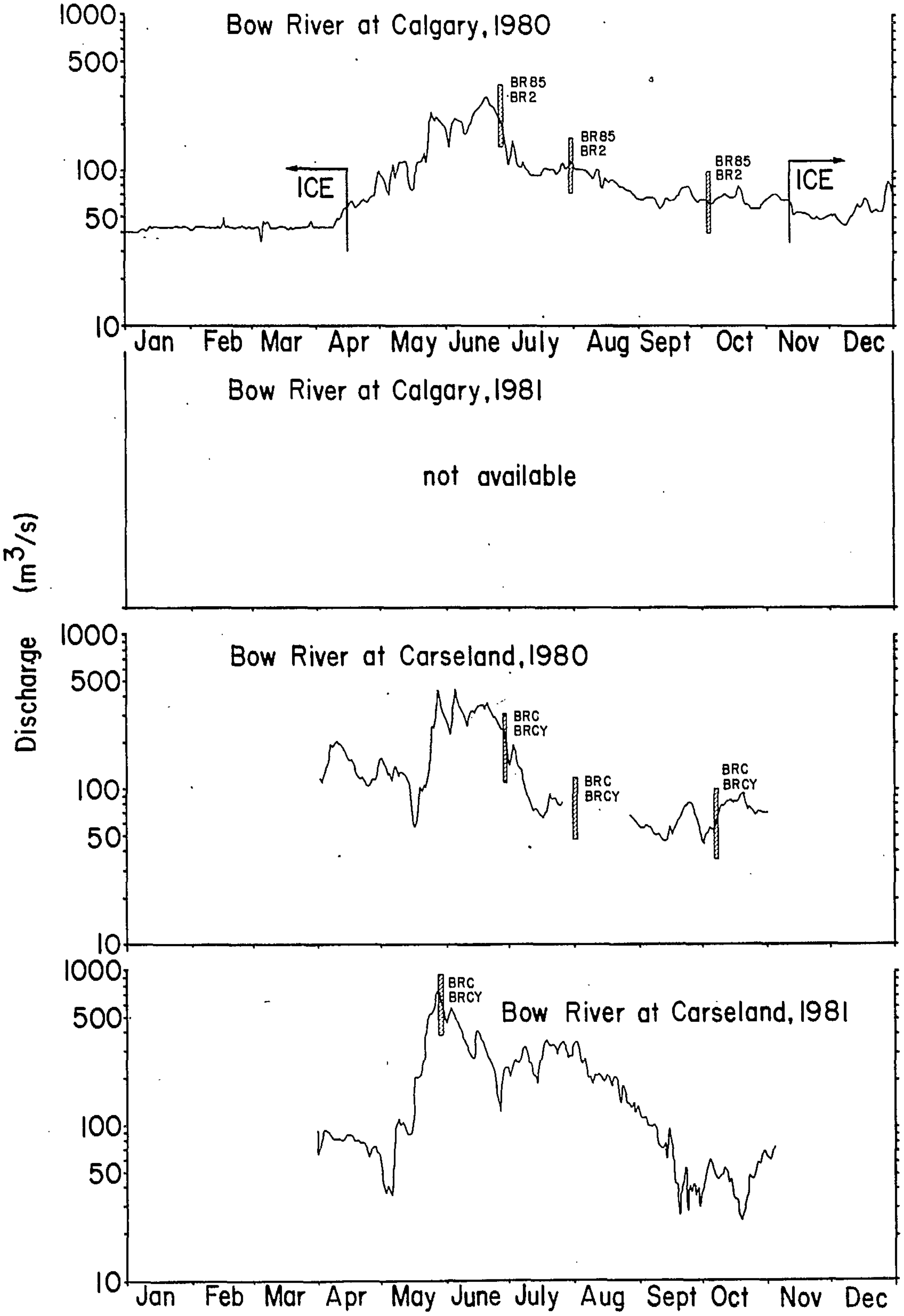


Figure 2. Discharge hydrograph for the Bow River at Calgary and Carseland. Sampling periods for the indicated sites are shown. (Water Survey of Canada)

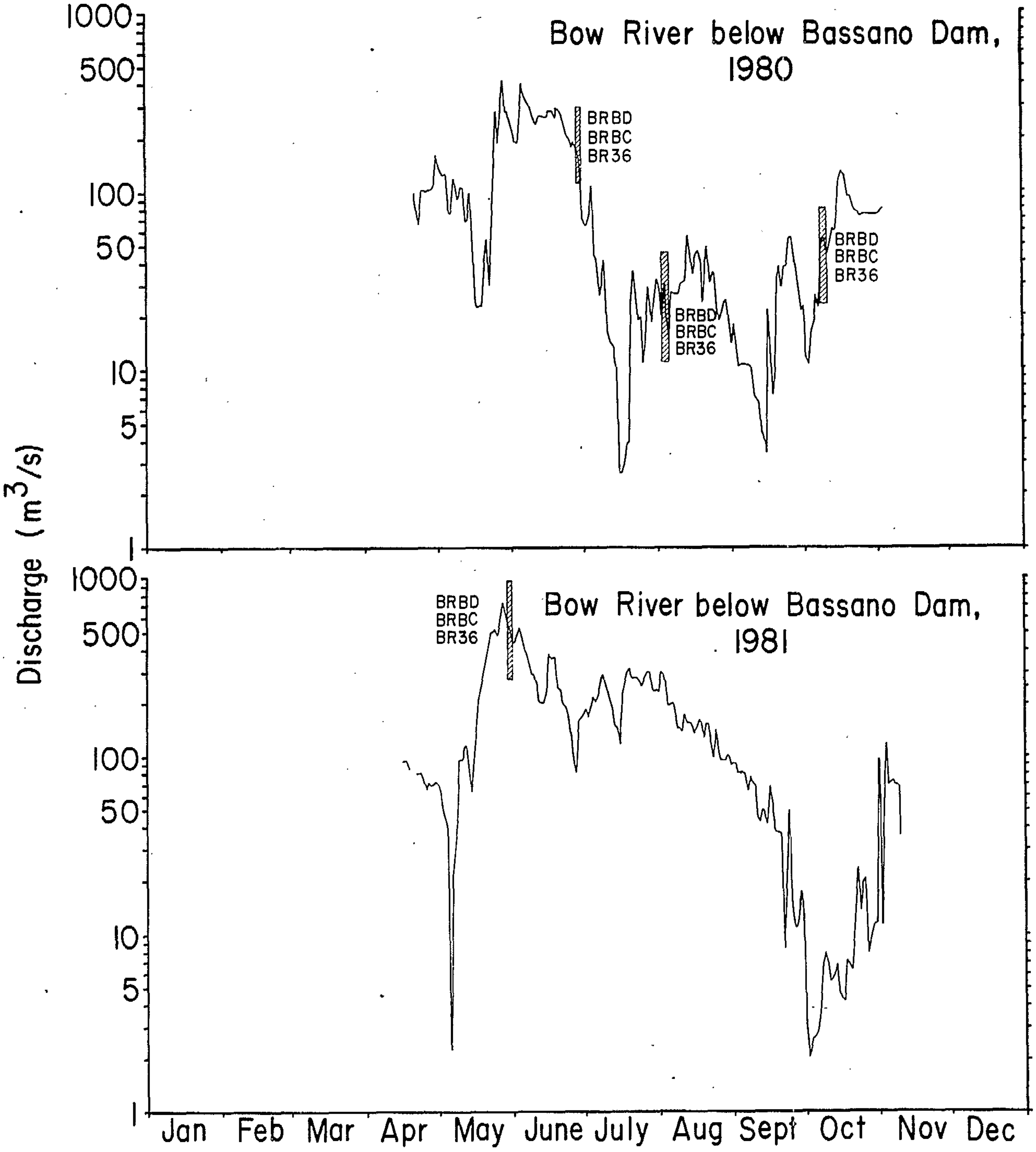


Figure 3. Discharge hydrograph for the Bow River at Bassano. Sampling periods for the indicated sites are shown. (Water Survey of Canada).

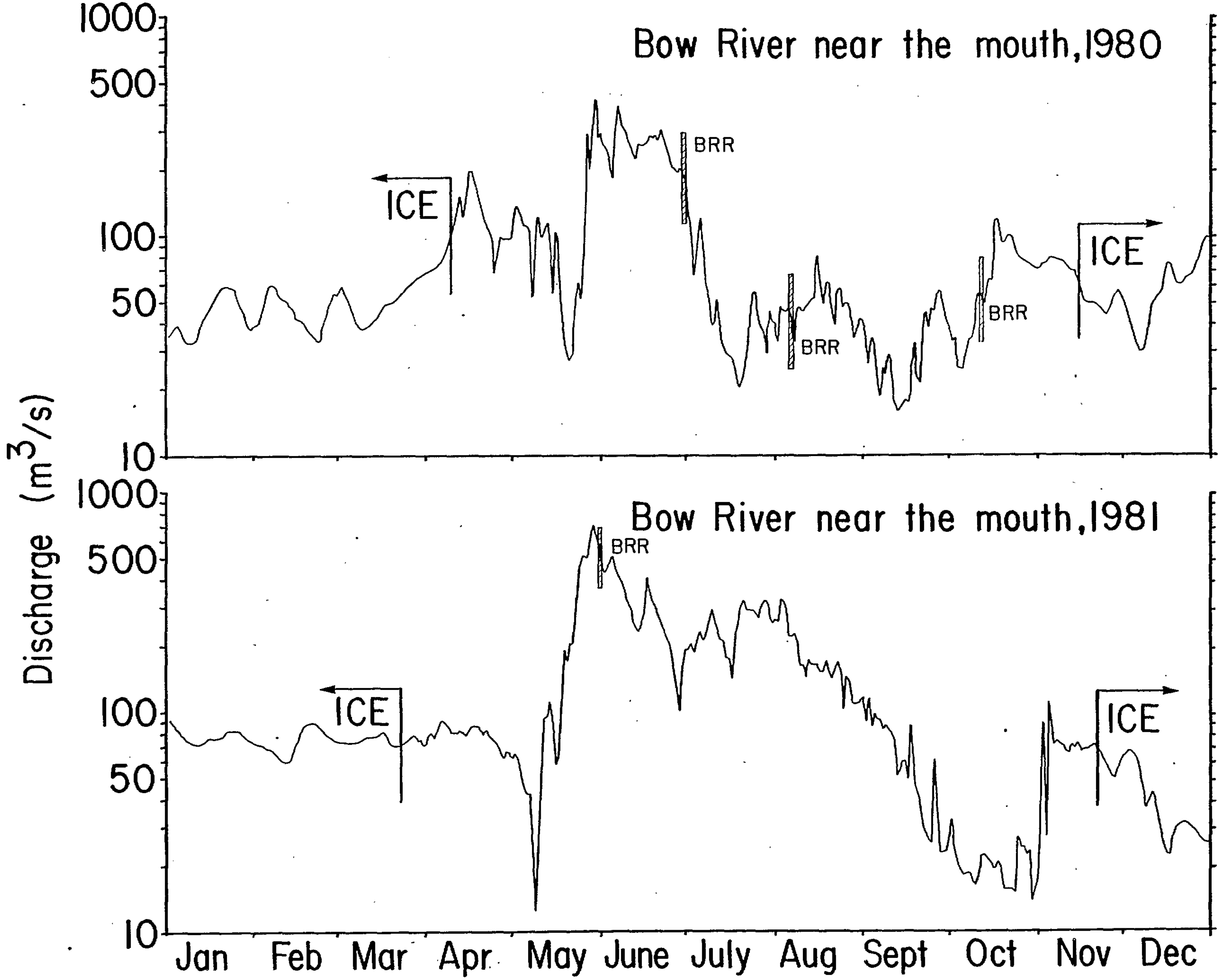


Figure 4. Discharge hydrograph for the Bow River near the mouth. Sampling periods for the indicated sites are shown. (Water Survey of Canada)

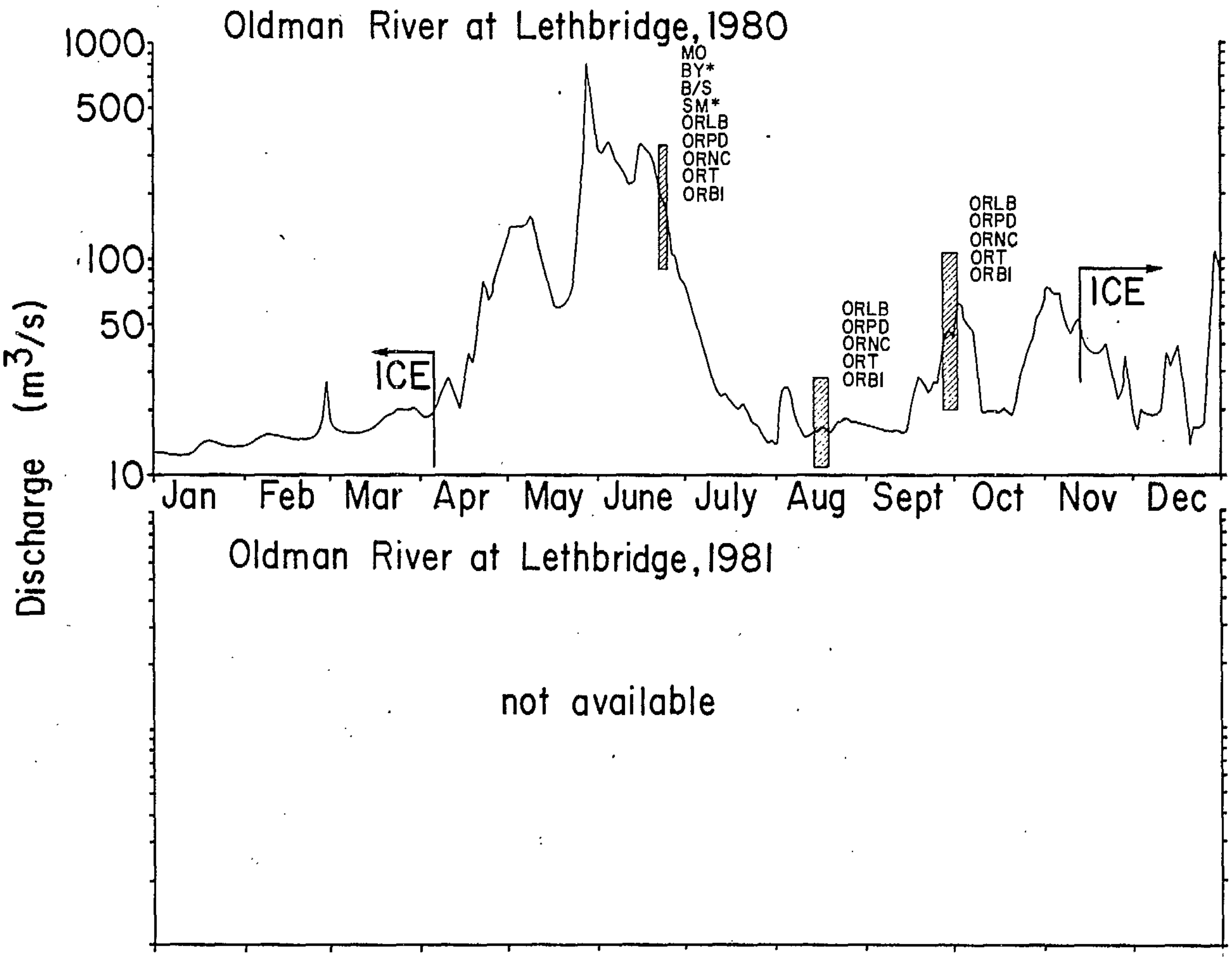
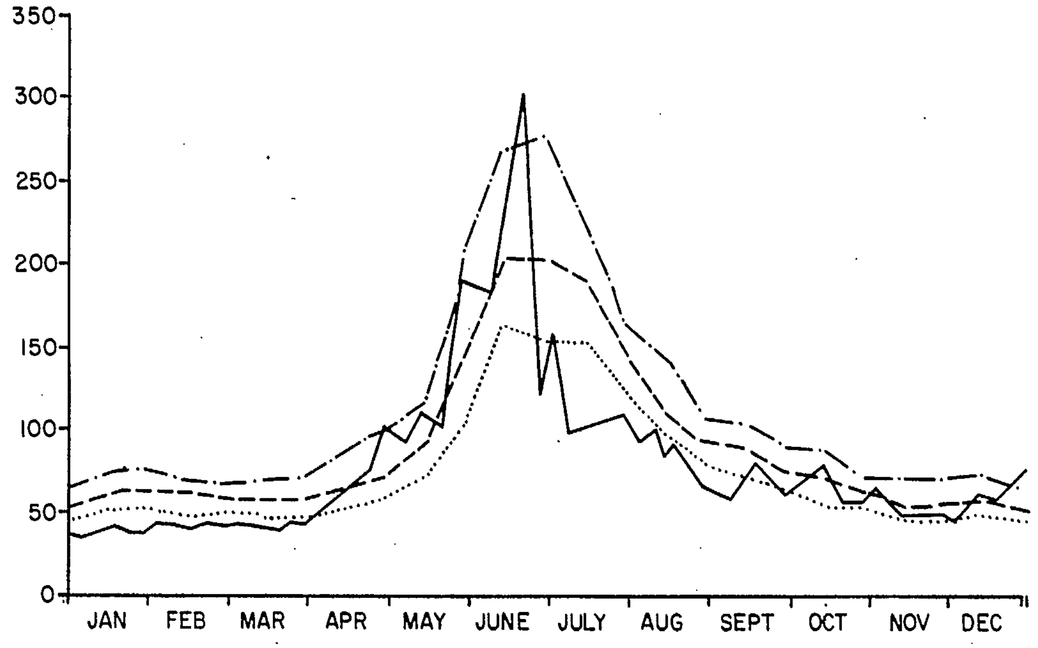
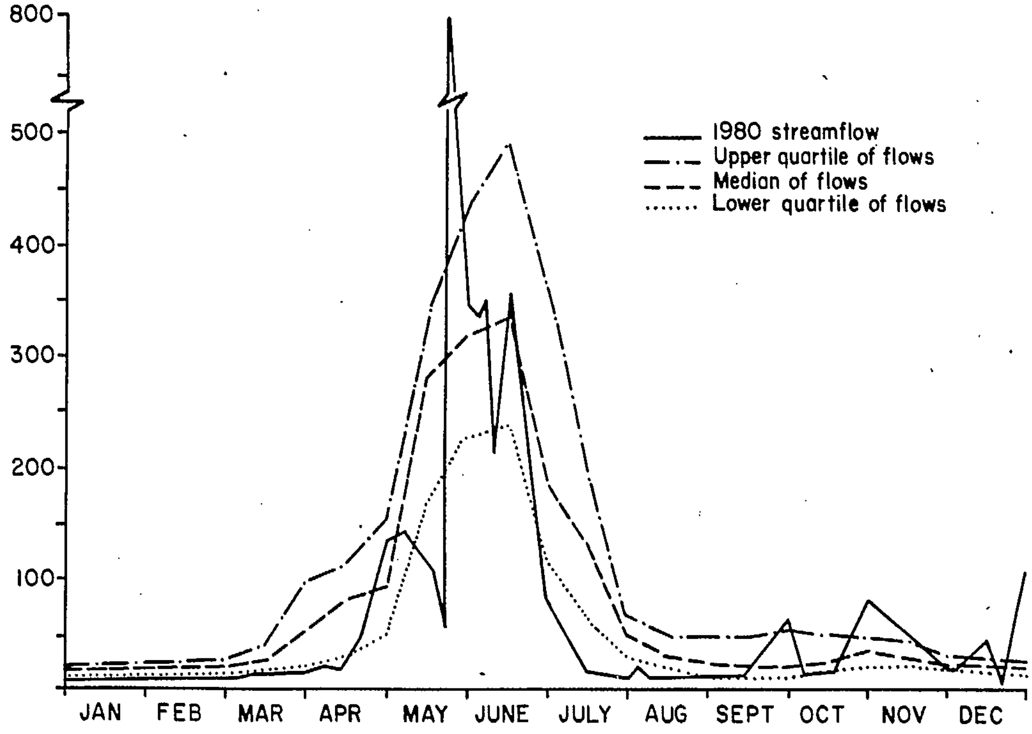


Figure 5. Discharge hydrographs for the Oldman River at Lethbridge. Sampling periods for the indicated sites are shown. (Water Survey of Canada).

BOW RIVER AT CALGARY, 1980



OLDMAN RIVER NEAR LETHBRIDGE, 1980



Note: Upper quartile, median, and lower quartile of flows based on 1957-1977 period of record for the Oldman River and 1949-1977 for the Bow River.

Figure 6. Historical discharge hydrographs for the Bow River at Calgary and the Oldman River near Lethbridge. (Water Survey of Canada).

the primary river sites during the early summer, summer, fall and spring regimes and at the auxiliary sites as noted above. Plant materials were collected only at primary sites and only during summer and fall of 1980 to reflect the major periods of productivity.

Irrigation return flows were sampled once every two to three weeks (Table 4) from June to September, 1980. The sampling schedule was built around equipment requirements of the river sampling program hence sampling intervals were not regular. Water samples were collected at all sites, however suspended sediment was collected only at those sites having observable turbidity (Table 4).

Water Samples

Water samples for metal analysis were collected into Nalgene polypropylene bottles. For rivers, two samples per section were collected near the surface, representing sample positions one-third and two-thirds the distance across the river section. In some instances due to excessive velocities or depths, samples were restricted to the vicinity of the intake pump of the continuous-flow centrifuge. Water was collected from irrigation return flows at mid-stream and at mid-point of the water column. Filtration was carried out in the field, initially using borosilicate glass funnels, then Sartorius polystyrene filtering funnels to reduce field breakage problems. Filtration was through a Gelman glass-fiber filter (to remove coarse sediment) placed on a Millipore 0.45 um membrane filter. Total and filtered water samples were acidified with concentrated nitric acid to produce a final concentration of 2.0 ml/L and stored at 4^{o}C. A number of replicates of total and filtered water were taken during the field program.

Sample bottles were pretreated by soaking in 3M HNO_3. for a minimum of one week; these were subsequently rinsed with distilled water and soaked for up to two months prior to use in a solution of 2 ml/L HNO_3. All filtering apparatus was soaked in 3M HNO_3 for a minimum of 12 hr between field filtrations and was rinsed immediately prior to use with 1.0% HNO_3 followed by distilled water, then river water.

Distilled water carried for field use was sampled at each site as

TABLE 3: River Sampling Schedule for Phosphorus, Trace Metals & Organochlorine Residues 1980-81 Date/Variables

	June/80	July-August/80	Sept-Oct/80	May/81		
Bow River	*	*	*	*		
BR85	26/6	29/7P,OCw..... Hg,w p	3/10 P,OCwp..Hg,w p	25/5 P,OCs..Hg,ws		
BR2	27/6	30/7 P,OCwsp...Hg,wsp	4/10 P,OCwp..Hg,wsp	26/5 P,OCs..Hg,ws	27/5 OCw	
BRC	28/6	31/7 P,OC(w)sp.Hg,wsp	5/10 P,OCwp..Hg,wsp	27/5 P,OCs..Hg,ws		
BRCY	28/6Hg,s	1/8 P,OC(w)sp.Hg,wsp	6/10 P,OCwsp.Hg,wsp	28/8 P,OCs..Hg,ws		
BRBD	29/6	2/8 P,OC(w)sp.Hg,wsp	7/10 P,OCwp..Hg,wsp	29/5 P,OCs..Hg,ws		
BRBC	29/6	4/8 P,OCw.....Hg,wsp	9/10 P,OCws..Hg,wsp	30/5 P,OCs..Hg,ws		
BR36	30/6Hg,s	5/8 P,OCwp....Hg,w p	10/10 P,OCwp..Hg,wsp	30/5 P,OCs..Hg,ws		
BRR	30/6Hg,s	6/8 P,OCwp....Hg,wsp	11/10 P,OCws..Hg,wsp	31/5 P,OCws.Hg,ws		
Oldman River	*	*	*	*		
ORLB	22/6Hg,s	13/8 P,OCw.....Hg,ws	26/9....OCws..Hg,ws	19/5 P,OCs..Hg,s	22/5 Hg,w	
ORPD	23/6Hg,s	14/8 P,OCwp....Hg,wsp	27/9..P,OCwsp.Hg,wsp	20/5 P,OCs..Hg,s	22/5 Hg,w	02/6 OCw
ORNC	23/6Hg,s	15/8 P,OCwp....Hg,wsp	28/9..P,OCws..Hg,wsp	21/5 P,OCs..Hg,s	22/5 Hg,w	
ORT	24/6Hg,s	16/8 P,OC(w)p..Hg,wsp	29/9..P,OCwsp.Hg,wsp	21/5 P,OCs..Hg,s	22/5 Hg,w	
ORBI	24/6Hg,s	18/8 P,OCwp....Hg,w p	1/10..P,OCwsp.Hg,wsp	22/5 P,OCs..Hg,ws	01/6 OCw	

Auxiliary Sites	*
MO	22/6/80
BY	22/6/80
B/S	22/6/80
SM	22/6/80
JP (Jumping Pound Creek)	24/5/81 Hg,s
CH (Bow R. at Cochrane)	24/5/81 Hg,s

Bank Samples (background)				
ORPD	20/5/81	Tot.Metals & Phos.	Hg	(bedrock)
ORBI	22/5/81	Tot.Metals & Phos.	Hg	(bedrock)
BRBD	29/5/81	Tot.Metals & Phos.	Hg	(bedrock)
BRBC	30/5/81	Tot.Metals & Phos.	Hg	(?alluvium)

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* : All sites/all dates: total & filtered metals and phosphorus; centrifuged suspended sediment for heavy metals and phosphorus.

P : Plants collected for metals and phosphorus analysis.

( ): Samples broken in transit.

OCwsp: Organochlorine analyses for w=raw water, s=centrifuged suspended solids, p=plants.

Hg,wsp: Total mercury for w=raw water, s=centrifuged suspended solids, p=plants.

TABLE 4: Irrigation Return Flow Sampling Schedule (Trace Metals and Organochlorine Residues): 1980 Date/Parameters

	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6
Piyami Drain (P.D.)	June 16 T/F SS	July 1 T/F SS	July 14 T/F SS	July 24 T/F SS	August 8 T/F SS OCw Hg,ws	Sept.20 T/F SS OCw Hg,ws
Little Bow R. (L.B.R.)	June 17 T SS	July 2 T/F SS	July 14 T/F SS	July 26 T/F SS	August 9 T/F SS OCw Hg,ws	Sept.20 T/F SS OCw Hg,ws
Expanse Coulee (E.C.)	June 17 T SS	July 2 T/F SS	July 16 T/F SS	July 25 T/F SS	August 9 T/F SS OCw Hg,ws	Sept.22 T/F SS OCw Hg,ws
New West Coulee(N.W.C.)	June 18 T SS	July 3 T/F SS	July 16 T/F SS	July 25 T/F SS	August 9 T/F SS OCw Hg(w)s	Sept.22 T/F SS OCw Hg,ws
Rolling Hills (R.H.)	June 18 T SS	July 3 T/F SS	July 16 T/F	July 24 T/F	August 10 T/F OCw Hg,w	Sept.21 T/F OCw Hg,w
Twelve Mile Coulee(T.M.C.)			July 16 T/F	July 24 T/F	August 10 T/F OCw(Hg,w)	Sept.21 T/F OCw Hg,w
Coal Creek (C.C.)	June 19 T	July 4 T/F	July 17 T/F	July 25 T/F	August 10 T/F OCw(Hg,w)	Sept.21 T/F OCw Hg,w
Cairn Hill Spillway (C.H.S.)	June 19 T SS	July 4 T/F SS	July 17 T/F SS	July 26 T/F SS	August 11 T/F SS OCw Hg,ws	Sept.24 T/F SS OCw Hg,ws

T/F : Total and filtered metals
SS : Centrifuged suspended solids for heavy metals + Hg/Se analyses
OCw : Organochlorine analysis for w=raw water samples
Hg,ws: Total mercury for w=raw water, s=centrifuged suspended solids
( ) : Samples broken in transit

a check on potential contamination. Distilled water for field use was prepared in the laboratory by passing single-distilled water through an IWT Research Model ion exchange cartridge to produce water with a conductivity of 0.3 umhos.

Water samples for phosphorus, mercury and organic contaminants were collected as close to mid-stream as possible. Pre-treated bottles for phosphorus and mercury were supplied by Alberta Environment and the Freshwater Institute respectively. Raw water for organic contaminant analysis was collected directly into 1000 ml amber Boston round glass bottles which had been prewashed in distilled-in-glass acetone and baked overnight at 280 °C. Bottle caps were lined with acetone-cleaned teflon and covered with acetone-rinsed aluminum foil. Each bottle contained 100 ml of dichloromethane and was shaken end-over-end for five minutes following sample collection. This procedure, which enhances preservation of organic contaminants which must be stored at 4 °C for lengthy periods prior to analysis, reflects experience of the Pesticide Laboratories of the Ontario Ministry of Environment and the Ontario Research Foundation.

Water for metal analysis (Fe,Mn,Ni,Pb,Zn,Co,Cd,Cu,Cr) was concentrated tenfold then digested with hot concentrated HNO_3. Samples were subsequently leached with 10% HCl then analyzed by flame atomic absorption spectrophotometry. Duplicates, blanks and prepared standards were included in the analysis. Calibration solutions were prepared by serial dilutions of stock solutions of known metal content to match the solution matrix of the analyte.

Total-P and Total Dissolved-P in water was determined by Alberta Environment. Total mercury was analyzed at the National Water Research Institute, Winnipeg; one complete season (spring/81) was collected and analyzed in duplicate. Organochlorine analysis was performed in duplicate using gas-liquid chromatography under varying packed column and capillary conditions by the Ontario Research Foundation (under contract).

Sediment Samples

Bulk samples of suspended sediment (organic + mineral) were quantitatively recovered in the field with an Envirodata Sedisamp continuous-flow centrifuge system (Ongley & Blachford, 1982). Whether operating from a boat (June, August runs), from shore (Oct.) or from a bridge (May), the centrifuged sample was pumped from just under the water surface and within the main flow of the river, usually 1/4 to 1/3 of channel width away from one of the banks (depending upon accessibility and the influence of upstream shore effects). Sampled sites were well downstream of point sources or tributary inputs to ensure complete mixing across the section. An established centre-stream pumping system (an Alberta Environment monitoring station) was used at site BR2 (Figure 1). Very occasionally heavy concentrations of sand required that input water to the centrifuge be passed through a bucket to allow coarse mineral material to settle out which would otherwise clog the centrifuge.

Field centrifugation was carried out at a flow rate of 4 L/min., a rate which experience has shown to maximize recovery efficiency under varying conditions of particle-size distribution, viscosity, organic content and input sediment concentration. Recovery efficiency was calculated at each site by the weight difference of 0.45um membrane filters through which an aliquot of input and output water had been vacuum filtered. Recovery efficiency characteristics established from these and other samples taken from rivers in western Canada are illustrated in Figure 7 (Ongley & Blachford, 1982).

Field centrifuged samples were transferred as a slurry to acid-rinsed/distilled-water soaked/river water rinsed 500 ml Nalgene bottles. The slurry was not acidified to avoid desorbing metals from the solids. The slurry samples were held at 4 ^{o}C for up to 24 hours, then bench centrifuged to recover the solids; the supernatant was discarded. The solid material was frozen and later freeze-dried. Centrifuged samples for organochlorine determination were removed from the field centrifuge as a sludge, wrapped in acetone-rinsed aluminum foil, and frozen.

Organic content of suspended sediment was estimated by loss on ignition on small subsamples. River sediments were oven-dried at 105 ^{o}C then heated for one hour at 550 ^{o}C (Dean, 1974). The difference between the sample weights at the two temperatures is recorded as loss-on-ignition. For comparative purposes, a cross-section of oven-

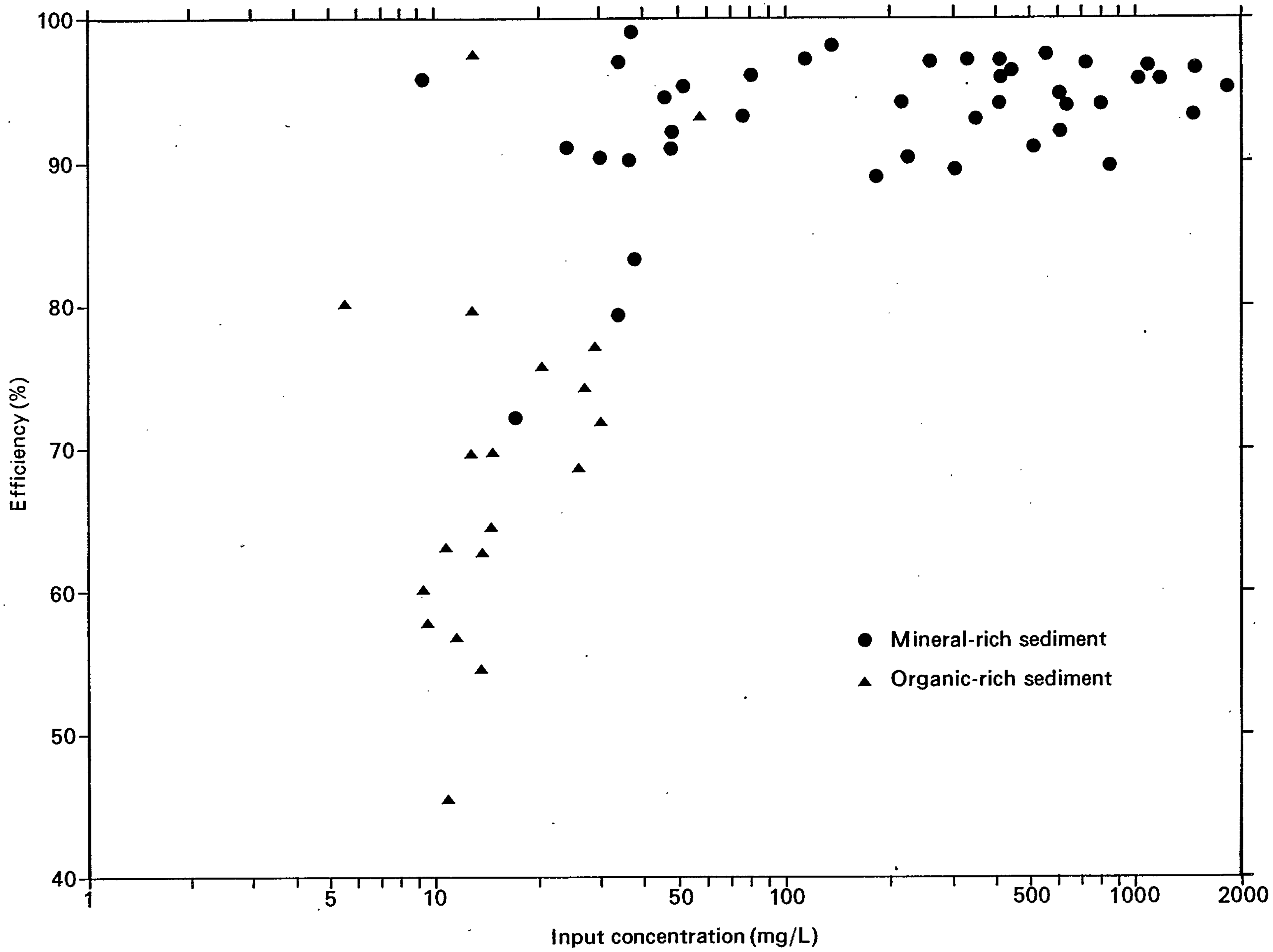

Figure 7. Recovery efficiency as a function of input suspended sediment concentration. Data are for a variety of rivers with a wide range of flow conditions and in different seasons of the year. Flow rate is 4 L/min. (after Ongley & Blachford, 1982).

dried samples was heated slowly to 450°C over a three hour period, and held at that temperature for one hour. Loss-on-ignition by this latter method was somewhat lower than values produced at 550°C. Organic content of suspended sediment from irrigation return flows was measured as loss-on-ignition after heating for one hour at 650°C (Konrad et al.,1970) and by the Walkley and Black (1934) method. Comparisons were made between replicates for each method and between methods. Generally, all loss-on-ignition methods produced roughly equivalent results. The Walkley and Black method produced significantly lower values.

Particle-size analysis was performed on all river and return flow sediments using a Micromeritics Sedigraph 5000D. Samples were analyzed as dispersed mineral aggregates and results are expressed as "equivalent settling diameter". Because of very limited quantities of sediment available for many of the sites, especially from the summer and fall sampling runs, particle size was determined on the material remaining from the loss-on-ignition procedure (0.8 - 1.2g) using a 05% Calgon solution. The sample was stirred for approximately one hour to ensure complete dispersion. A number of raw (freeze-dried) samples were treated with hydrogen peroxide (to eliminate organic matter) and dispersed in Calgon in order to ascertain the error associated with the use of loss-on-ignition residue. For these samples, both methods produced similar results.

All suspended sediments were analyzed for metals using a hot concentrated nitric acid - 10% hydrochloric acid digestion. The method reflects the amount of total metal present in the sample with the exception of metals bound in the silicate lattice of clay minerals. Because total decomposition of silicates is unlikely to occur in the natural environment of the study area this analytical procedure is a satisfactory approximation of total metal concentrations on solids. Measured concentrations of metals were prorated onto the silt-clay fraction of the sample following particle-size analysis.

Additional metal extractions were carried out on a selection of the irrigation return flow sediment samples. Selective extractions attempt to characterize various metal associations with solid matter. These additional extractions were: room-temperature 10% HCl (to ascertain the necessity of hot concentrated HNO_3); room-temperature 2.5% HCl (carbonate-bound metals); and a 1.0M $MgCl_2$ extraction in an acid medium ("exchangeable" fraction). Geological standards, blanks and duplicates were included in all analyses. Serial dilutions were prepared from a multi-element standard solution for calibration purposes.

Phosphorus fractionation on suspended sediment was performed using the Williams <u>et.al.</u> (1976) method. The procedure requires that a sample be partitioned into two subsamples. The first is analyzed for apatite phosphorus(AP) and non-apatite phosphorus (NAIP) (by the sum of two fractions); the second subsample is analyzed for total phosphorus, inorganic phosphorus and organic phosphorus (OP) (by difference). The analytical method is based upon the complexation of phosphate with molybdate molecules in an acid medium. The resulting compound is reduced with ascorbic acid to produce a blue colour which is measured spectrophotometrically.

Suspended sediment was analyzed for total mercury and organochlorine compounds by Dr.A.Lutz of the Freshwater Institute, Winnipeg, and the Ontario Research Foundation respectively.

Although the quantity of suspended sediment recovered in summer and fall sampling runs was small, it was possible to assess certain samples for major elements (as oxides) by X-Ray Fluorescence (Fe_2O_3, TiO_2, CaO, K_2O, MnO, SiO_2, Al_2O_3, MgO, P_2O_5, Na_2O). Sediments were heated at 1000°C with lanthanum oxide and lithium tetraborate to produce a fused bead. The bead was then ground to a fine powder with a cellulose binding material (Avicel) and pressed into a pellet on a borax layer for XRF analysis. Results are reported in Appendix 1.

A selection of bank samples was collected during the spring/81 run to assess the background chemistry of sediments introduced as suspended matter by bank collapse. Bank samples represent poorly consolidated bedrock and alluvial floodplain deposits. Bank sampling was not intended to be a comprehensive study of bank materials; it does, however, give some idea of typical values for comparison with the chemistry of suspended sediment. Bank samples were analyzed for metals, organic content, particle size and common elements.

Aquatic Plants: A representative collection of biomass was taken at all primary river sites during the summer and fall runs. The Bow river is dominated by rooted macrophytes with some filamentous algae. The Oldman River tends to be dominated by filamentous algae with some macrophytes. Macrophytes and algae were collected, where possible, across each river site and over a reach of up to two kilometers where plant material was sparse. Where a single species colonized a section, a composite sample was taken. Where a variety of species were present, each was sampled individually. Plants were identified by species, gently rinsed in river water to remove loosely entrapped particulate matter, then dried at less than 50°C on acetone-rinsed aluminum foil. At some sites where there was abundant plant material, samples were divided into roots, mid-plant and node sections.

Plant materials were ground to a powder in a Wiley mill and analyzed for heavy metals, phosphorus fractions, and organochlorine compounds using the same methods as for suspended sediment. Replicates were analyzed to establish precision and, for heavy metals, results were compared with orchard leaf standards.

PHYSICAL CHARACTERISTICS OF SUSPENDED SEDIMENT

The physical characteristics of suspended sediment are an important variable in the geochemical transport of nutrient and contaminant forms in aquatic systems. Seasonally-variant concentrations of suspended sediment, particle-size characteristics and associated geochemistry have a significant impact on water chemistry. For geochemical purposes it is the <62 um fraction which is of significance due to large surface area of clay-size (<2 um) and colloidal materials.

The organic content of suspended sediment may be a quantitatively significant component of the particulate load during periods of major biomass accumulation. Luxury uptake of nutrients, heavy metals and contaminants leads to concentrations of these elements several orders of magnitude above that found in ambient water. Organic colloids display strong adsorptive properties. Qualitatively, then, the organic fraction appears to be disproportionate in its contribution to chemical activity of the total sediment load.

Particle Size

The organic/inorganic composition and particle-size fractions of the suspended sediment samples collected over the various flow regimes of these prairie rivers are presented in Figure 8. The height of the bar in each histogram corresponds to sediment concentration; the size fractions represented within each bar are the proportions by weight, of each particle-size category.

The sediment in early summer on the Bow river is predominantly in the silt range (62 - 2 um). Clay (<2um) is noticeably present while the organic and sand fractions are of minor importance. Summer and fall sediments show an increase in the proportion of organic solids and a decrease in the silt portion. The fall samples show a marked increase in clay content. Spring samples are characterized by similar quantities of silt and clay with small amounts of sand and organic

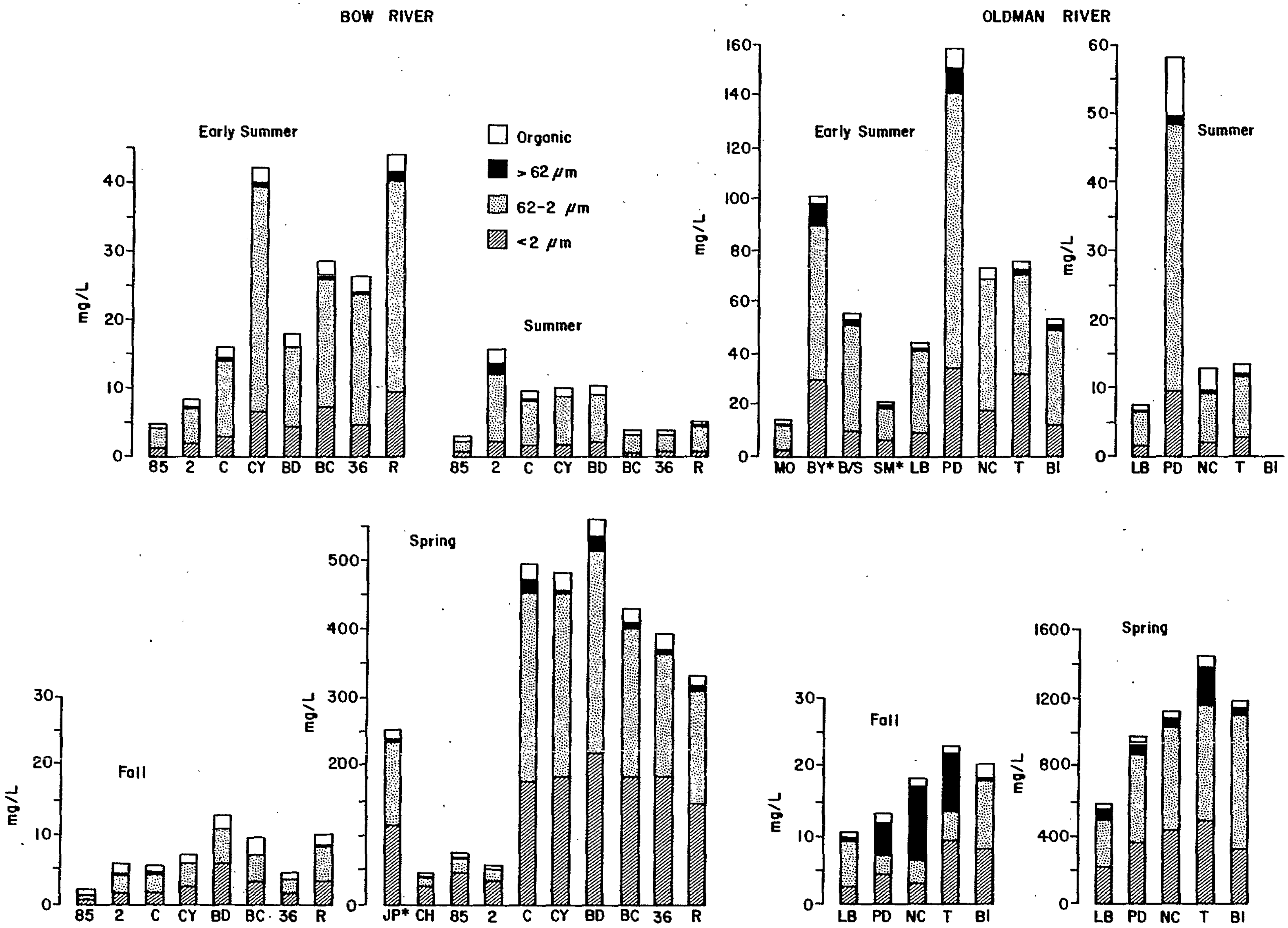

Figure 8. Suspended sediment concentrations and organic/mineral fractions of the sediments. The height of each bar represents the total sediment concentration. The organic component and the sand(>62um), silt(62-2um), and clay(<2um) components of the mineral material are indicated as proportions of the total sediment concentration.

matter. The sediment concentration in the spring (+/-500 mg/L) is an order of magnitude greater than that in any other season and has a profound effect on river chemistry. Early summer concentrations are less than 45 mg/L; summer and fall concentrations are less than 15 mg/L. Downstream trends in particle size and sediment concentration are discussed below.

Sediments in the Oldman River have a high silt content in early summer, diminishing in the summer and fall as the organic content increases. The proportion of clay increases in fall and, surprisingly, in spring. The large sand fraction in the fall probably reflects disturbance in the river as a result of construction at ORNC and ORT and is probably not typical of fall sediments at those sites. A significant quantity of sand in the spring sediment samples reflects increased solids transport associated with a high energy regime. Sediment concentrations in the spring are an order of magnitude greater than in the early summer which are, in turn, an order greater than those in the summer and fall. Here, as for the Bow River, high spring and early summer sediment concentrations exert a strong influence on aquatic chemistry.

Sediment concentrations were approximated by two methods. An original estimate was derived from the weight of sediment collected by the centrifuge, prorated by the flow rate and sample period, and corrected for recovery efficiency. A second estimate was obtained by gravimetric determination of a filtered aliquot of centrifuge input water through a 0.45 um filter. The sediment concentrations noted in Figure 8 are those found by the first method. Both methods have inherent errors. Flow rates to the centrifuge are not always maintained at 4 L/min over the period of pumping due to field difficulties such as cavitation of the pumps (during boat operations) and temporary blocking of pump intakes by organic debris. Recovery efficiency is determined by gravimetric differences between filtered input and output water though 0.45 um membrane filters. This can lead to substantial error in recovery efficiency estimates, especially when the input concentration is very low. Nevertheless, errors in this first method are probably commensurate with errors inherent in instantaneous samples and in gravimetric procedures, especially for low values of concentration. The first method produces a time-integrated average whereas the latter is an instantaneous estimate. For all of these reasons, low levels of sediment concentration, as in the summer and fall for the Bow and summer for the Oldman, should be regarded as less reliable than higher concentrations in other seasons.

For geochemical purposes, it is only the <62 um fraction which is of interest. Although the vertical distribution of <62 um is known to be independent of depth, total sediment concentration is very much depth dependent. Values reported here are taken near the surface and at a single location within the section (generally 1/4 to 1/3 distance from an accessible bank). Suspended sediment concentrations reported here cannot, therefore, be meaningfully applied to total suspended concentrations but are adequate for the subsieve fraction of geochemical interest in this study.

Organic Content

Loss-on-ignition results for river sediments are illustrated in Figure 9. Dean (1974) found good correlation between percent loss on ignition and percent organic content for calcareous sediment samples. Experience with alternative methods of ignition indicates that this procedure leads to over-estimation and should only be regarded as a relative measure of organic content.

The organic content of Bow River sediments is distinctly higher in the summer and fall (times of major biomass production) than earlier in the year. Organic peaks are clear at BR2 and BR36 in the fall. Spring results show a minor increase at BR2 while the early summer trend is characterized only by a minor decrease at BRCY.

Oldman River sediments show no trends in organic content in the spring and early summer when suspended mineral concentrations are high. In the fall, values are somewhat higher with rises at ORPD and ORBI. Summer values are distinctly elevated, coinciding with the period of bioproductivity, and peak at ORNC and ORBI.

Figure 10 illustrates major seasonal differences in the combined effects of organic content and particle size (expressed as silt/clay ratio) for the geochemically active subsieve fraction for both rivers. Seasonal differentiation was also observed by Ongley <u>et al.</u> (1981) for

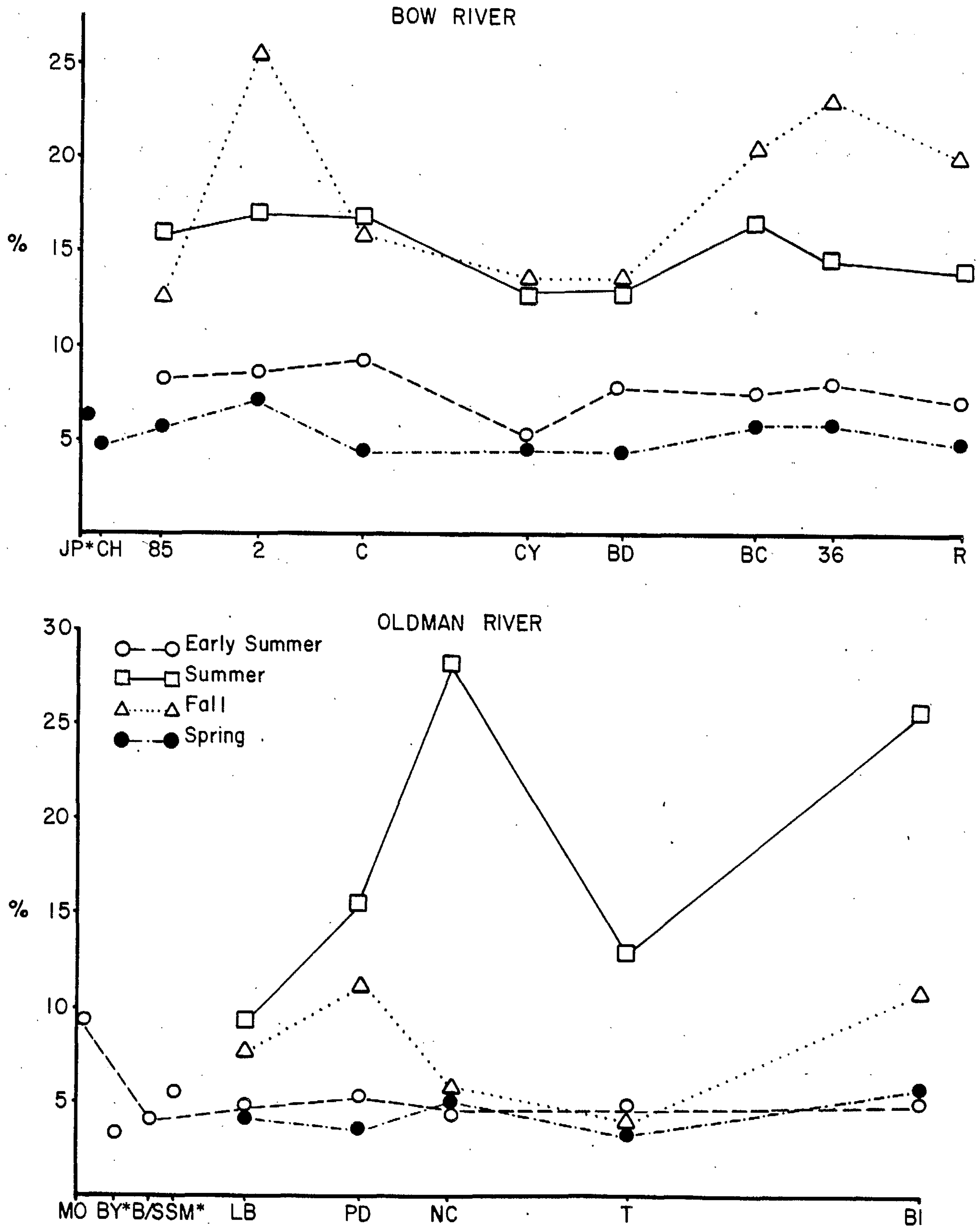

Figure 9. Suspended sediment organic content for the Bow and Oldman Rivers. Determined by % loss-on-ignition (Dean, 1974).

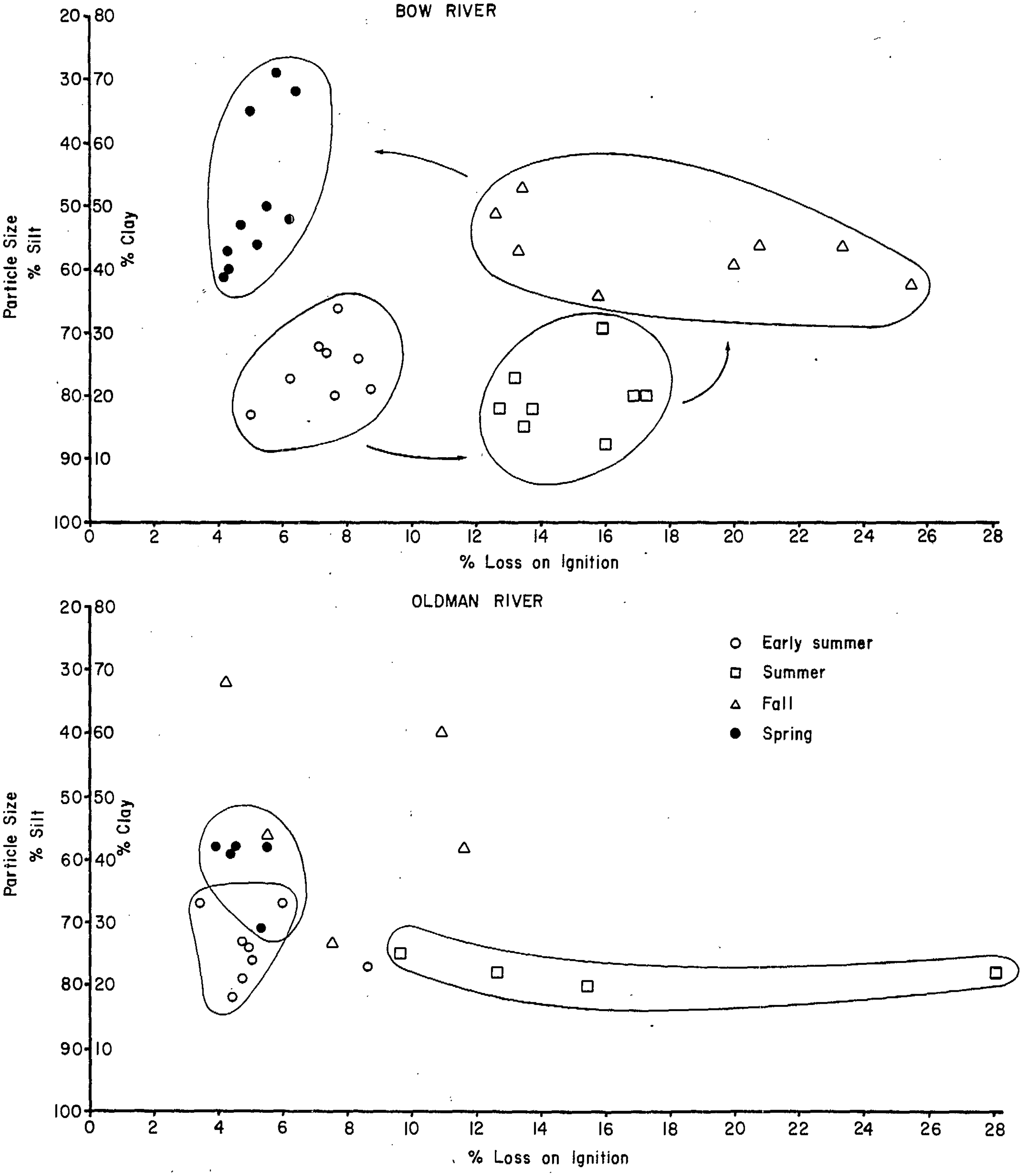

Figure 10. Seasonality of particle size and organic content of suspended sediments. The silt/clay ratio is calculated from the portion of mineral sediment <62um. Organic content determination by % loss on ignition.

a small nonpoint source catchment of eastern Ontario.

Bow River sediments in early summer have small amounts both of organic and silt-size material. Organic content increases in summer and more so in fall when the proportion of clay also rises, reflecting biomass production and inability of the low-flow regime to transport coarse-grained mineral particles. Spring data are characterized by a high percent of clay (reflecting surface erosion processes) and low quantities of organic matter.

Seasonality of sediment properties, although not as distinct in the Oldman River as for the Bow, are similar. Unlike the Bow, fall sediments in the Oldman are highly variable.

PHOSPHORUS

Phosphorus concentrations in water and suspended sediments in the Bow and Oldman Rivers are presented in Figures 11 & 12. Diagrams are arranged to reflect the order in which sampling occurred - early summer/´80, summer/´80, fall/´80, spring/´81. The diagrams indicate two estimates for Total-P; one is the summation of the individual phosphorus fractions and the other (open bar)is an independent determination of Total-P. The difference in these two values is an indication of analytical variance. Phosphorus levels in aquatic plants are presented after the discussion of water and sediment.

Bow River: Water

Phosphorus in Bow River water (Figure 11) shows variation in total concentration, particulate and dissolved proportions and downstream trends among the seasons. Water in spring/81 contains greater concentrations of total phosphorous than in other seasons, reflecting diffuse source runoff from large contributing areas of the basin. The phosphorus load is largely (>10%) in particulate form due to the high concentration of suspended sediment during the spring. Dissolved phosphorus concentrations are at a uniformly low level as a result of dilution by the high spring flow.

In early summer total phosphorus concentrations are lower, reflecting reduction in diffuse source contribution and lower sediment concentrations; substantially less phosphorus is in particulate form. Dissolved concentrations are greater as the total volume of flow is reduced. It is worth noting that the percent of total phosphorus in particulate form during the high flow regimes remains quite constant from BRCY to BRR (>90% in spring and 37-58% in early summer).

Summer and fall waters have slightly higher total phosphorus concentrations that in early summer. The reduced flow conditons and sediment concentrations result in a greater proportion of the total phosphorus falling in the dissolved phase with reduced amounts in

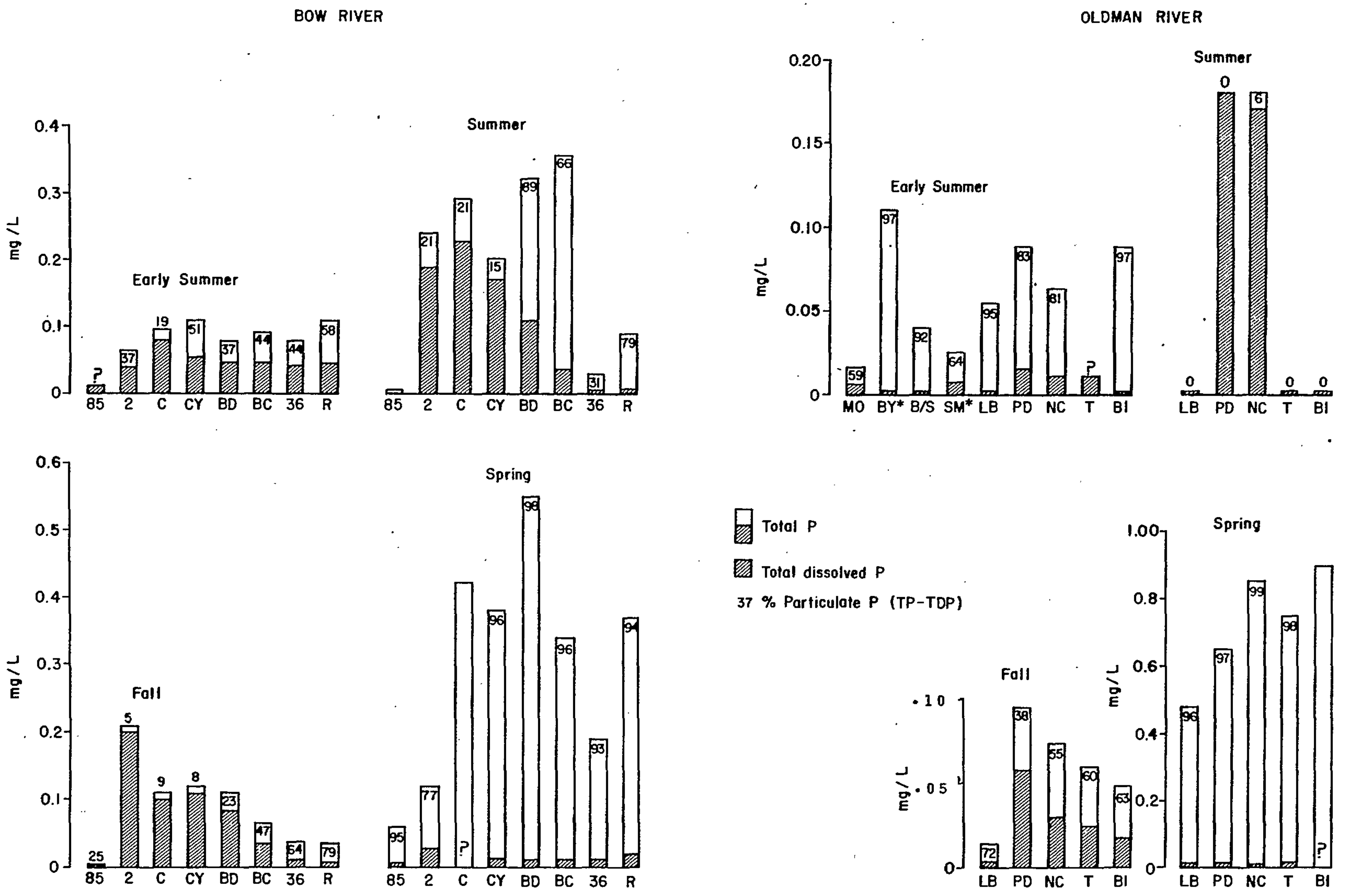

Figure 11. Total and Dissolved phosphorus concentrations in Water. The particulate fraction is calculated as the difference between Total and Dissolved P. Particulate P is presented numerically as a percentage of Total-P. Missing fractions are denoted by "?".

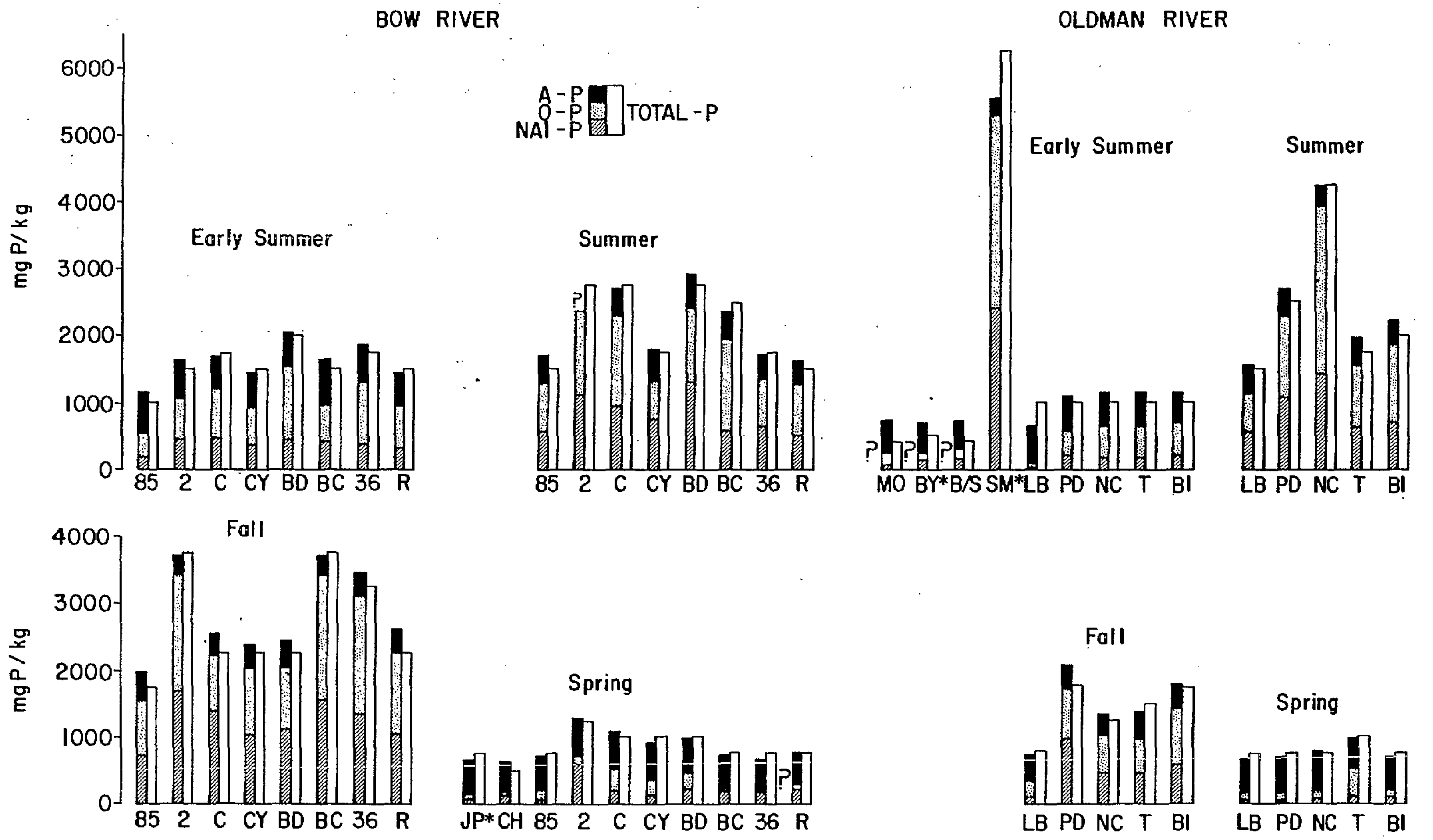

Figure 12. Phosphorus speciation on suspended sediments (Williams et al.1976). The amount of each phosphorus species can be calculated using the ordinate axis scale. The sum of the three species cannot be computed where one of the fractions is missing (denoted by "?"). Difference between TP and sum of NAI-P, O-P and A-P is a measure of analytic imprecision.

particulate form. The summer flow regime was unstable in 1980 owing to several rainstorm events which occurred during the sampling run and fluctuating extraction requirements for irrigation purposes at Bassano Dam. Downstream from Bassano water levels visibly rose and fell over a period of an hour or more. Fluctuating water levels tended to mobilize periphyton and rainstorm events produced local inputs of suspended sediment; together, these may account for the elevated levels of total phosphorus at BRBD, BRBC and BRR. These changes in flow did not affect dissolved phosphorus concentrations but resulted in a disproportionate particulate contribution to total phosphorus.

The fall samples were collected during a stable flow regime. Total and dissolved phosphorus concentrations decline steadily from BR2 to BRR. The downstream trend of declining dissolved phosphorus and increasing particulate phosphorus suggests a conversion from one form to the other. This is likely occurring through sorption of soluble orthophosphate ions onto mineral and organic surfaces, and precipitation of the ions to form compounds of low solubility. In view of a similar decline in soluble phosphorus from BR2 to BRR during summer, similar mechanisms may be assumed to occur during the entire low-flow period.

Bow River: Suspended Sediment-Associated Phosphorus

Fractionation of sediment-associated phosphorus shows strong seasonal differences in sediment source. Apatite-P comprises more than half the total phosphorus associated with sediments in the spring. The exception is BR2 where a larger portion of the phosphorus is NAI-P, presumably reflecting the influence of the Calgary STP. Apatite-P, a non-enriched background mineral phosphate produced from eroding prairie soils, dominates all sites in fairly constant proportions. Phosphorus speciation of bank materials collected at BRBD and BRBC is almost identical to that found at a non-enriched site (eg. CH, Figure 1). The lower Total-P concentrations in the spring reflect the large sediment loads having low background levels of sediment-associated phosphorus and which reduce the effects of anthropogenic NAI-P on a per weight basis. The moderate decline in Total-P downstream from BR2 refects decreasing amounts of NAI-P and O-P.

Early summer sediments contain an increased proportion of O-P and NAI-P and a much reduced amount of A-P. Total-P increases at BR2 show no apparent downstream trends. Phosphorus concentrations are higher than in the spring due to point source enrichment and a reduced quantity of sediment in transport.

Summer and fall sediments are further enriched as sediment concentrations decrease. The trends in Total-P in summer and especially in fall follow very closely the trends in organic content of the sediments. The Total-P increases at BR2, BRBC and BR36 in the fall are attributed to increases in the O-P fraction. Similarly, the decreases in O-P in summer from BRC to BRCY and from BRBC to BR36, parallel organic decreases in the solids. This suggests an organic solids contribution to the suspended sediment load upstream of BR2 (Calgary STP?) and additions to the suspended load of benthic material and/or algae at the downstream sites.

The proportion of A-P increases and Total-P decreases in summer and fall from BR2 to BRCY, likely due to dilution of enriched sediment observed at BR2 by tributaries further downstream carrying background levels of phosphorus in apatite form. This deduction is consistent with observations of reduction in metal concentrations on sediments at the same sites.

Oldman River: Water

Phosphorus concentrations in water of the Oldman River show similar patterns to those seen in the Bow River. Concentrations are highest in the spring when sediment concentrations are highest; the phosphorus load is almost entirely (>96%) associated with the particulate fraction. Dissolved phosphorus is uniformly low because of dilution by the very high flow.

In early summer phosphorus concentrations are reduced, reflecting the reduction in sediment input from diffuse sources at this time of year. The increased particulate fraction of Total-P at locations of higher sediment concentrations is most evident at BY*(Belly River tributary inflow) and ORPD. The higher proportion of particulate phosphorus in the Oldman River in early summer is a function of the relatively elevated sediment concentration and, in relative terms, the reduced impact of dissolved phosphorus contribution from Lethbridge to the Oldman than from Calgary to the Bow.

The high dissolved-P levels at ORPD and ORNC in summer reflect dissolved-P sources from Lethbridge and very reduced sediment concentrations. The exceedingly low levels of Total-P at ORT and ORBI appear suspect; such a large decline in phosphorus from ORNC to ORT does not appear reasonable.

Total-P in the fall rises at ORPD, then declines steadily downstream, an observation also made on the Bow. The conversion of dissolved-P to particulate form downstream from ORPD is not obscured by small increases in subsieve sediment concentration over the same reach. This conversion reflects uptake by biomass and is accompanied by an increase in NAI-P from ORNC to ORBI.

Oldman River: Suspended Sediment-Associated Phophorus

Like the Bow, sediment-related phosphorus in the Oldman River is dominated by background A-P in the spring. The constant proportions of the phosphorus fractions at all sites and their similarity to bank materials (collected at ORPD and ORBI) reflect a diffuse runoff source. Low Total-P values on sediment reflect influx of large quantities of sediments having a background level of phosphorus.

Compared with spring data, early summer sediments show a reduction in the proportions of A-P below Lethbridge. The O-P and NAI-P fractions, likely originating from phosphorus discharged from Lethbridge, appear to be responsible for the increase in Total-P downstream from Lethbridge. In contrast, above the point source of Lethbridge, A-P dominates the Total-P load and is similar to A-P concentrations in the spring with minimum amounts of NAI-P and O-P. Total-P and proportions of NAI-P and O-P are anomalously high in the St.Mary River (SM*); these have no ready explanation and do not affect the overall trend in the Oldman River after mixing has occurred below the point of confluence.

Sediment-P shows an increase from LB to ORNC in the summer and from LB to ORPD in the fall. Both rises are responses to increased O-P and NAI-P proportions. The trends in both seasons are identical to those in sediment organic content. This suggests biomass accumulation below Lethbridge and subsequent mobilization of enriched organic matter into the suspended sediment load.

Aquatic Plants

Phosphorus concentrations in aquatic macrophytes and filamentous algae are presented in Figure 13 for the Bow and Oldman Rivers. The small amounts of A-P and larger amounts of NAI-P associated with biomass are presumed to reflect entrapped suspended mineral matter, co-precipitates with calcium encrustations, etc.. Organic-P represents phosphorus assimilated into the plant and bound into the organic tissue of the plant in association with oxygen and carbon atoms.

Total-P concentrations in plants are higher (summer) or approximately equal (fall) to those found on suspended sediments in the Bow and exceed sediment-P concentrations for both seasons in the Oldman.

Downstream trends in aquatic plant-related phosphorus are not immediately apparent. The significant but varying proportions of inorganic-P at each site reflect the control exerted by plant size and structure, and the location and micro-environment within the river where the plant was sampled, upon quantity of entrapped mineral material. Total-P concentrations are not, therefore, a satisfactory measure of plant response to available phosphorus, nor as a measure of assessing spatial or temporal trends. The enrichment ratio (concentration factor) of phosphorus in plants, calculated as a ratio of O-P in plant to Total Dissolved-P, is a direct measure of phosphorus uptake (assuming that TDP is an appropriate surrogate for the available component of TDP). It usefully illustrates site differences in uptake by plants.

Enrichment ratios (Table 5 & Figure 11) and trends in TDP reveal interesting patterns. Changes in plant O-P are not directly parallel to changes in TDP as might be expected on the assumption that increased concentrations of available phosphorus should be reflected in parallel increases in O-P. In fact, plants appear to concentrate (luxury uptake) available phosphorus only in sufficient quantities to reach or maintain a relatively constant concentration. The average O-P concentrations for all plants sampled (macrophytes and filamentous

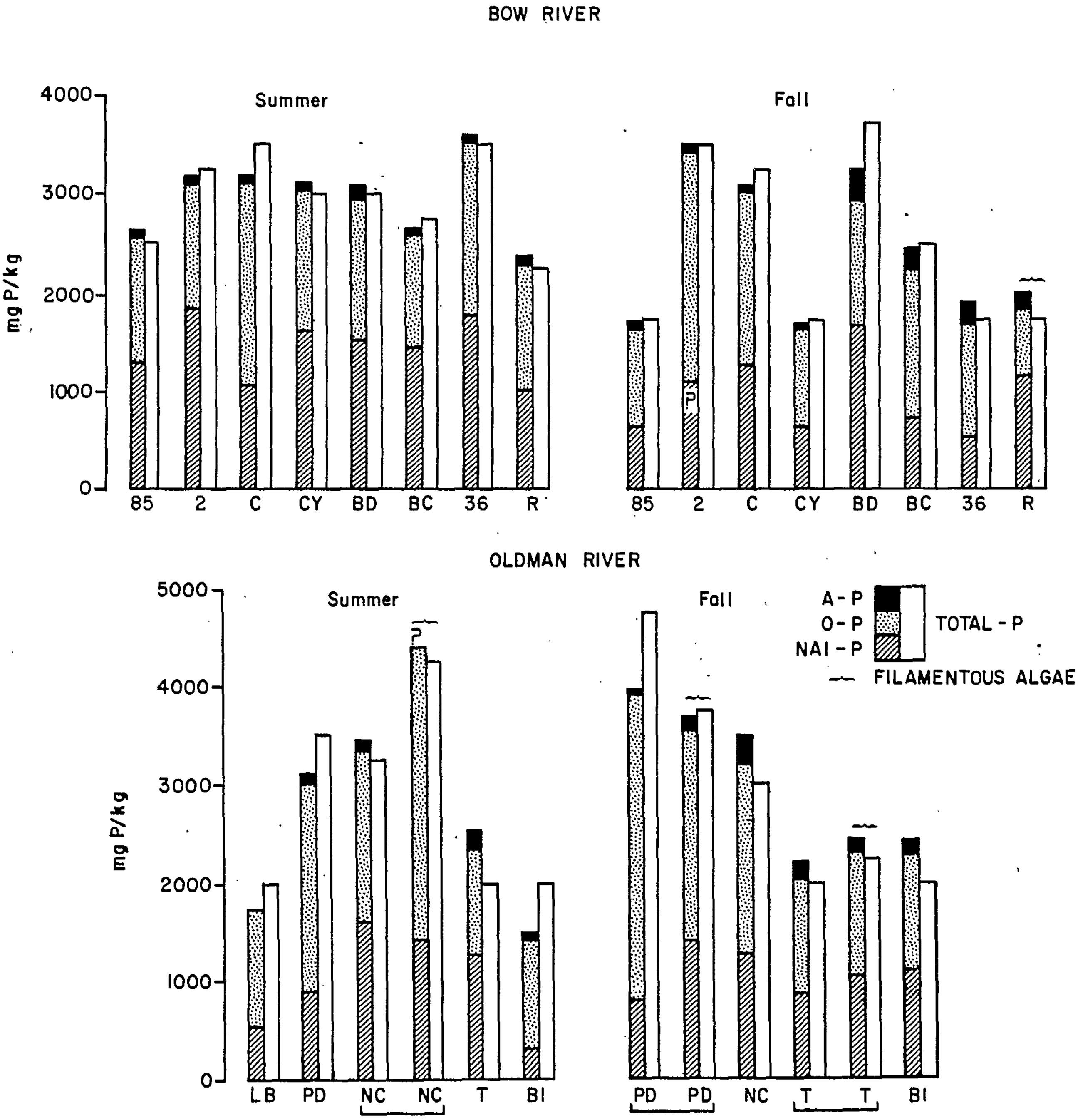

Figure 13. Phosphorus speciation in aquatic plants (Williams et al., 1976). The amount of each phosphorus species can be calculated using the ordinate axis scale. The sum of the three species cannot be computed where one of the fractions is missing. (denoted by "?"). Potamogeton sp. are represented unless otherwise indicated. Bars (⊔) show sites where macrophytes and algae are both represented.

TABLE 5: Organic Phosphorus in Plants

		mg/kg ORG-P in plants	ENRICHMENT RATIOS *	
			Org-P/TDP	Total-P(plant)/TDP
<u>Bow River</u>				
Summer	BR85	1250	>2.5 $x10^5$	>5.0 $x10^5$
	BR2	1300	6.8 $x10^3$	1.7 $x10^4$
	BRC	2050	8.9 $x10^3$	1.5 $x10^4$
	BRCY	1400	8.2 $x10^3$	1.7 $x10^4$
	BRBD	1425	1.3 $x10^4$	2.7 $x10^4$
	BRBC	1150	2.9 $x10^4$	7.1 $x10^4$
	BR36	1750	1.0 $x10^5$	2.1 $x10^5$
	BRR	1250	6.6 $x10^4$	1.2 $x10^5$
Fall	BR85	1000	3.3 $x10^5$	5.8 $x10^5$
	BR2	2350	1.2 $x10^4$	1.8 $x10^4$
	BRC	1750	1.7 $x10^4$	3.3 $x10^4$
	BRCY	1000	9.1 $x10^3$	1.6 $x10^4$
	BRBD	1250	1.5 $x10^4$	4.4 $x10^4$
	BRBC	1500	4.3 $x10^4$	7.1 $x10^4$
	BR36	1150	8.8 $x10^4$	1.3 $x10^5$
	BRR	~(700)	(1.0 $x10^5$)	(2.5 $x10^5$)
<u>Oldman River</u>				
Summer	LB	1200	4.0 $x10^5$	6.7 $x10^5$
	ORPD	2100	1.2 $x10^4$	2.1 $x10^4$
	ORNC	1750	1.1 $x10^5$	2.0 $x10^5$
		(2900)	(1.8 $x10^5$)	(2.7 $x10^5$)
	ORT	1100	3.6 $x10^5$	6.7 $x10^5$
	ORBI	1200	4.0 $x10^5$	6.7 $x10^5$
Fall	LB	-	--	--
	ORPD	3150	5.3 $x10^4$	8.1 $x10^4$
		(2100)	(3.5 $x10^4$)	(6.4 $x10^4$)
	ORNC	1950	5.9 $x10^4$	9.1 $x10^4$
	ORT	1150	4.6 $x10^4$	8.0 $x10^4$
		(1300)	(5.2 $x10^4$)	(9.0 $x10^4$)
	ORBI	(1150)	(6.4 $x10^4$)	(1.1 $x10^5$)

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* data from <u>Potamogeton</u> sp.

~( ) filamentous algae

algae) are approximately 1400 and 1600 mg/kg for the Bow and Oldman respectively. As a consequence, changes in TDP produce substantial changes in enrichment ratios.

As examples of variation in enrichment ratios, the dramatic decline in TDP in the summer from BRC to BRR is accompanied by only a minor decrease in O-P in plants over the same distance; as a consequence, there is a downstream increase in enrichment by an order of magnitude. Likewise, the decrease in TDP in the fall from BRCY to BRR produces no significant change in O-P but results in an order of magnitude increase in enrichment. A similar observation applies to the Oldman River biomass in both seasons. In summary, plants living in a phosphorus-rich environment have lower enrichment factors and only show an increase in O-P close to the phosphorus source (BR2). In contrast, plants in a phosphorus-poor environment maintain average levels of O-P and display large enrichment ratios. This observation has immediate consequences for interpreting biomass control strategies in nutrient-rich rivers.

Implications for Biomass Control

The observation that levels of O-P in plants remain at a relatively constant level (1400 - 1600 mg/kg) regardless of TDP levels indicates that measures of O-P in plants are not useful indicators of nutrient stress. Stress is manifested in productivity (size) of individual plants and density of the plant community within a reach. Elevated nutrient conditions appear to create favourable growth conditions in the Bow River. The appearance and, probably, density of aquatic plants especially in lower reaches of the Bow, appears to be controlled by re-seeding of opportunistic species originating from areas of luxurious growth upstream. Once established, the size of plant (rate of growth,etc.) is controlled by ambient level of phosphorus. Measures of productivity and plant cover are appropriate indicators of nutrient stress in an environment where equilibrium has been established between average nutrient conditions and population propogation. Where extreme perturbation in environmental conditons has occurred, such as the large flows which destroyed the dense plant community in the lower Bow in early 1980, the deduction of low nutrient stress based on observed productivity would be highly misleading. As an example, the assumption of low potential for dense plant growth in the lower Bow based upon 1980 and 1981 observations of productivity is probably false, mainly because the system was highly perturbed the preceeding spring. Although nutrient conditions in the downstream reach is close to background (ie. compared to BR85), community propagation originating from more nutrient-rich environments upstream would appear to be an inevitable consequence as long as dense macrophyte populations are allowed to survive in areas close to Calgary.

The ability of plants to rapidly accumulate nutrients to levels in excess of their immediate requirements (luxury uptake) allows the plant to survive periods of nutrient deficiency. If the low TDP values observed in the lower Bow in summer and fall of 1980 are typical of values in earlier years, the luxuriant plant growth in earlier years may well reflect the ability of plants to rapidly accumulate nutrients during brief periods of nutrient flux. If true, macrophyte control strategies will require, therefore, the suppression of brief contaminant pulses from point sources.

METALS

Concentrations of ten metals (Fe, Ni, Cd, Co, Mn, Cr, Pb, Zn, Cu, Hg) in water, suspended sediment and aquatic plants are presented in Figures 14 to 23 for the Bow and Oldman Rivers. Seasonal and phase differences in concentration, downstream trends, comparisons between the rivers and the information provided by monitoring each of the water, suspended sediment and plant phases are discussed.

Bow River: Water

Understanding the seasonal and downstream contribution of Total and Filterable metals in water to biogeochemical cycling mechanisms is hindered by the fact that most filterable and many Total metals exist at concentrations below conventional detection limits. Detectable Total Mn, Ni, Fe, Cu, Zn, Cr & Hg are found in the Bow River in spring whereas only Mn and Cu can be detected in filterable form. Spring metal levels tend to be approximately ten-fold higher than concentrations in any other season. Exceptions to this are Ni (not detectable in other seasons) and Hg (spring levels exceed levels in other seasons by $<$ x2).

The difference in metal concentrations between spring on the one hand, and all other seasons is attributed mainly to large differences in suspended sediment concentrations and to changes in the particle-size distribution of sediment between seasons. Spring sediment concentrations are more than an order of magnitude larger than in other seasons and are comprised of a larger proportion of fines (Figure 8). Physical characteristics also explain the downstream trends in metal concentrations. Sediment concentrations escalate in spring from below 100 mg/L at upstream sites to more than 500 mg/L at sites further downstream due to large inputs from several tributaries (especially Highwood River and Arrowwood Creek) and from large-scale bank collapse. There is a parallel trend in the clay-size fraction (Figure 8). These features coincide with relatively low Total metal concentrations at BR85 and BR2 and much higher concentrations from BRCY

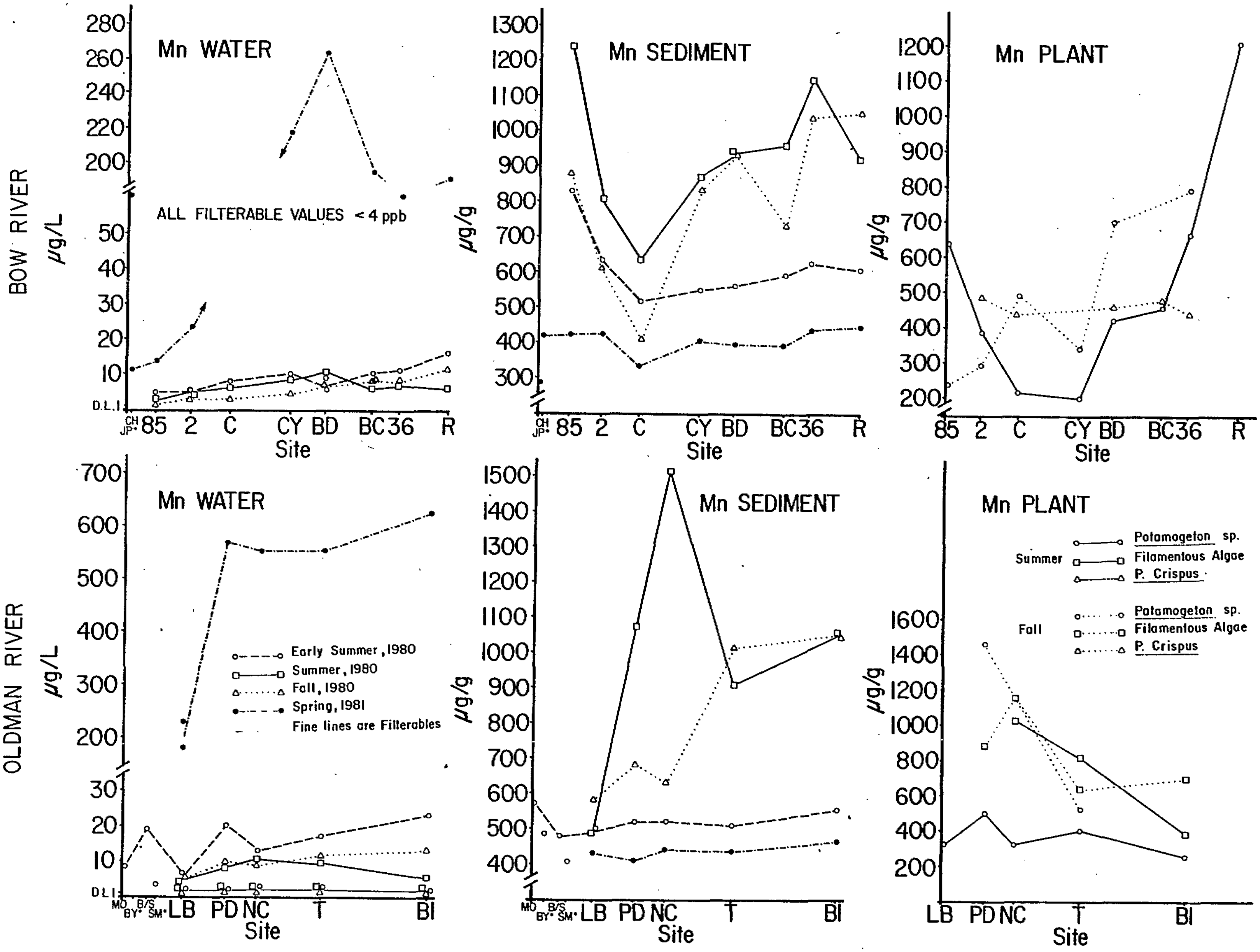

Figure 14. Manganese concentrations in water, suspended sediment and plant phases for the Bow and Oldman Rivers. Distance between sites on graphs is proportional to actual river distances.

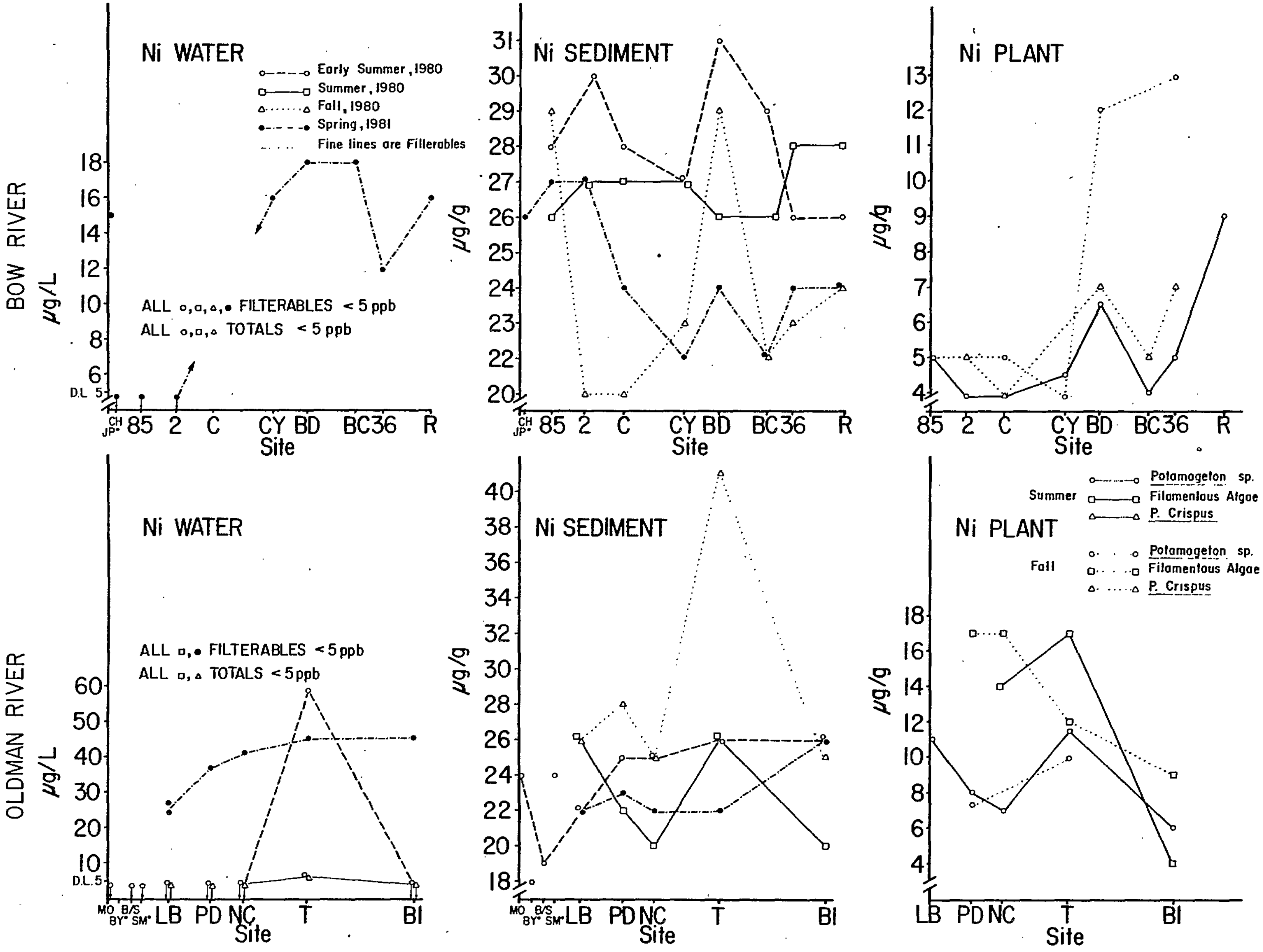

Figure 15. Nickel concentrations in water, suspended sediment and plant phases for the Bow and Oldman Rivers. Distance between sites on graphs is proportional to actual river distances.

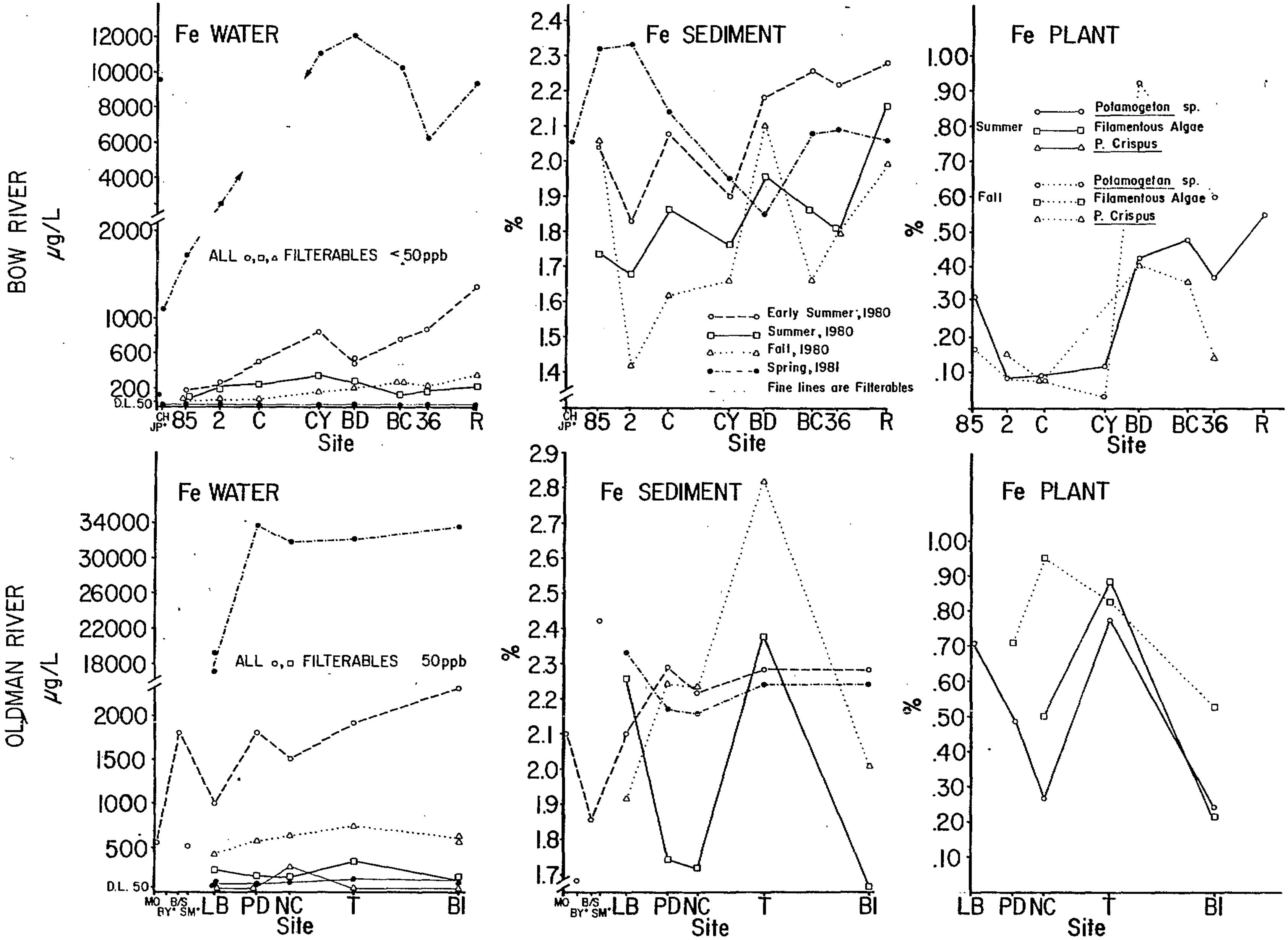

Figure 16. Iron concentrations in water, suspended sediment and plant phases for the Bow and Oldman Rivers. Distance between sites on graphs is proportional to actual river distances.

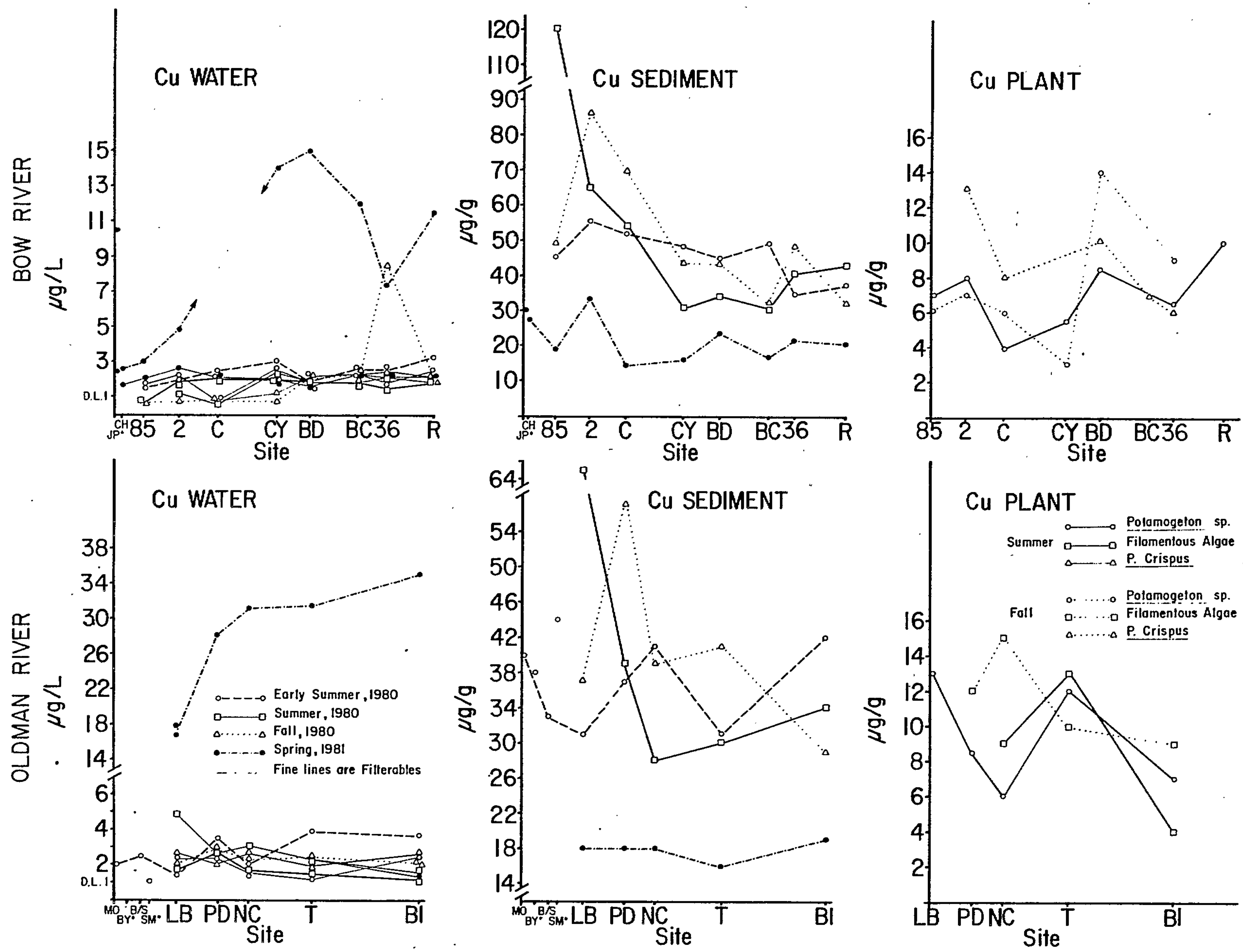

Figure 17. Copper concentrations in water, suspended sediments and plant phases for the Bow and Oldman Rivers. Distance between sites on graphs is proportional to actual river distances.

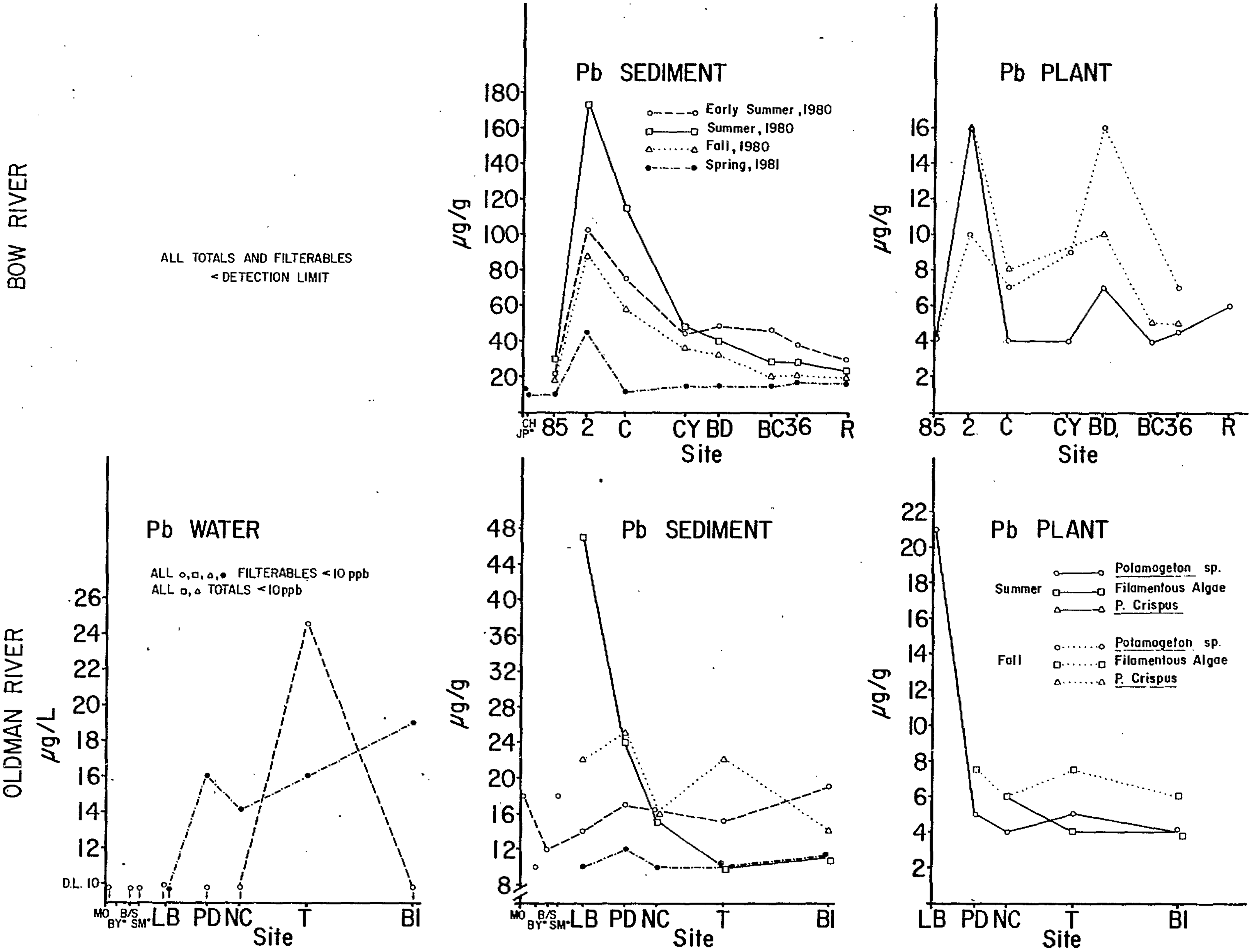

Figure 18. Lead concentrations in water, suspended sediment and plant phases for the Bow and Oldman Rivers. Distance between sites on graphs is proportional to actual river distances.

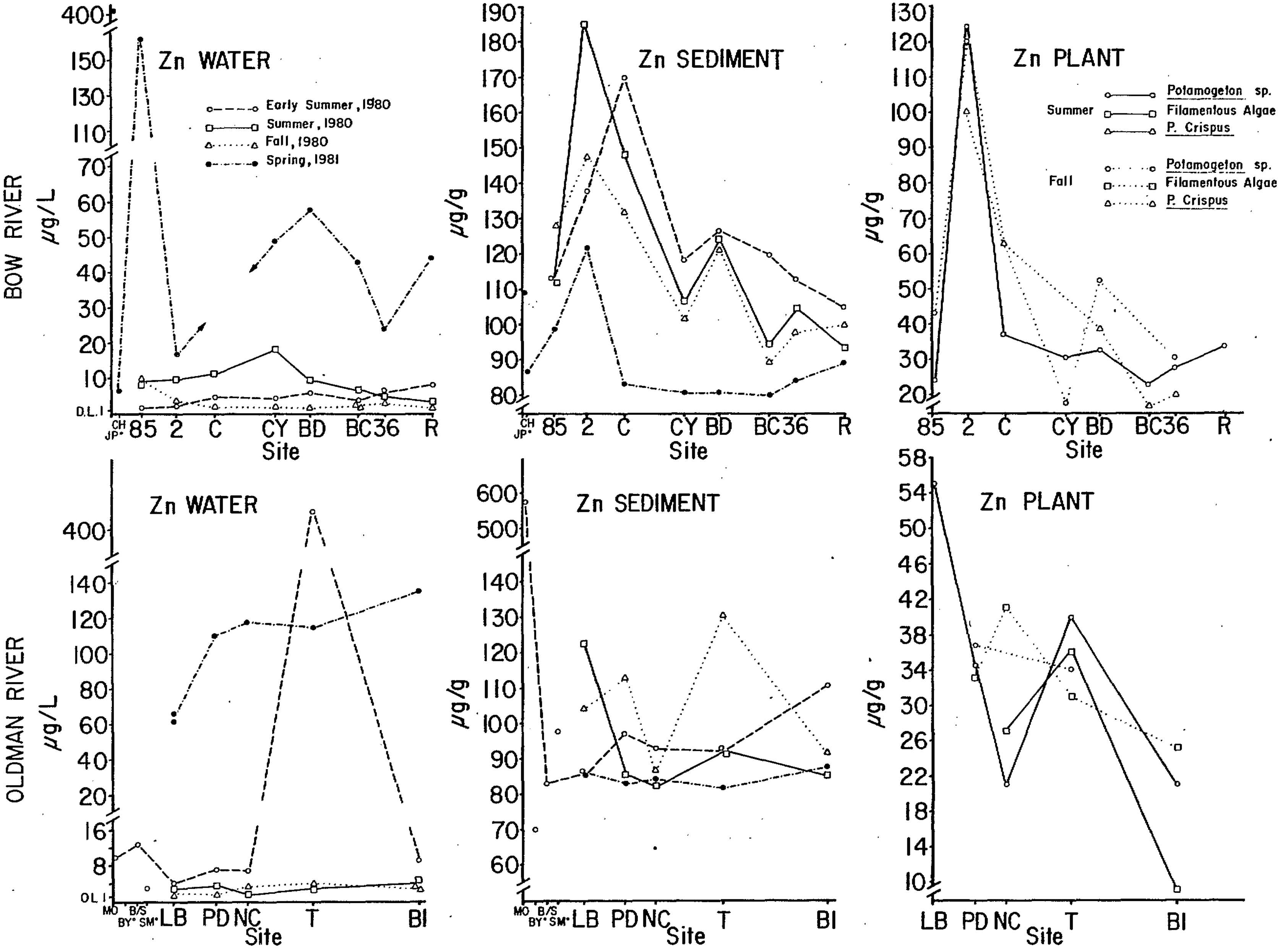

Figure 19. Zinc concentrations in water, suspended sediment and plant phases for the Bow and Oldman Rivers. Distance between sites on graphs is proportional to actual river distances.

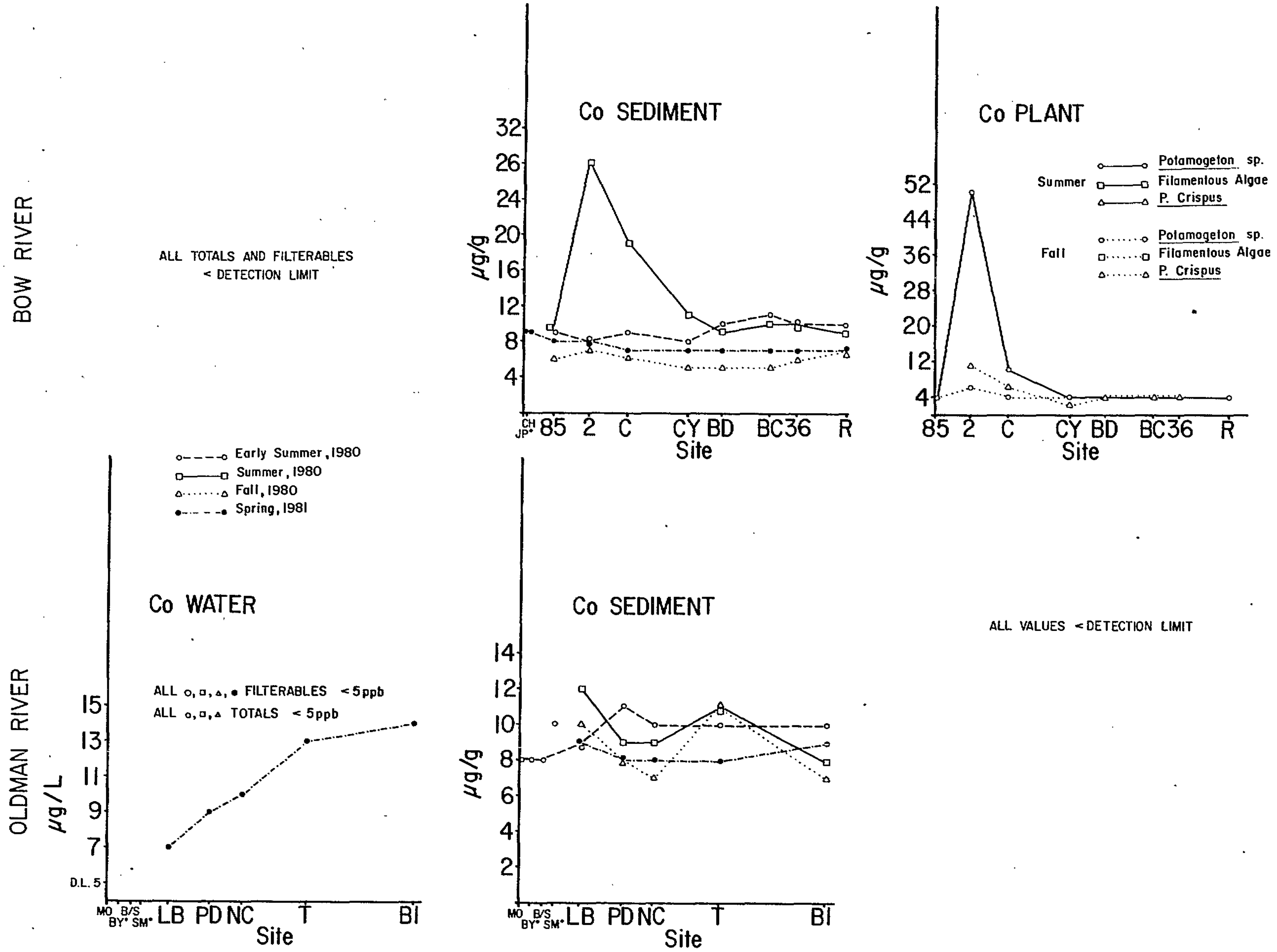

Figure 20. Cobalt concentrations in water, suspended sediment and plant phases for the Bow and Oldman Rivers. Distance between sites on graphs is proportional to actual river distances.

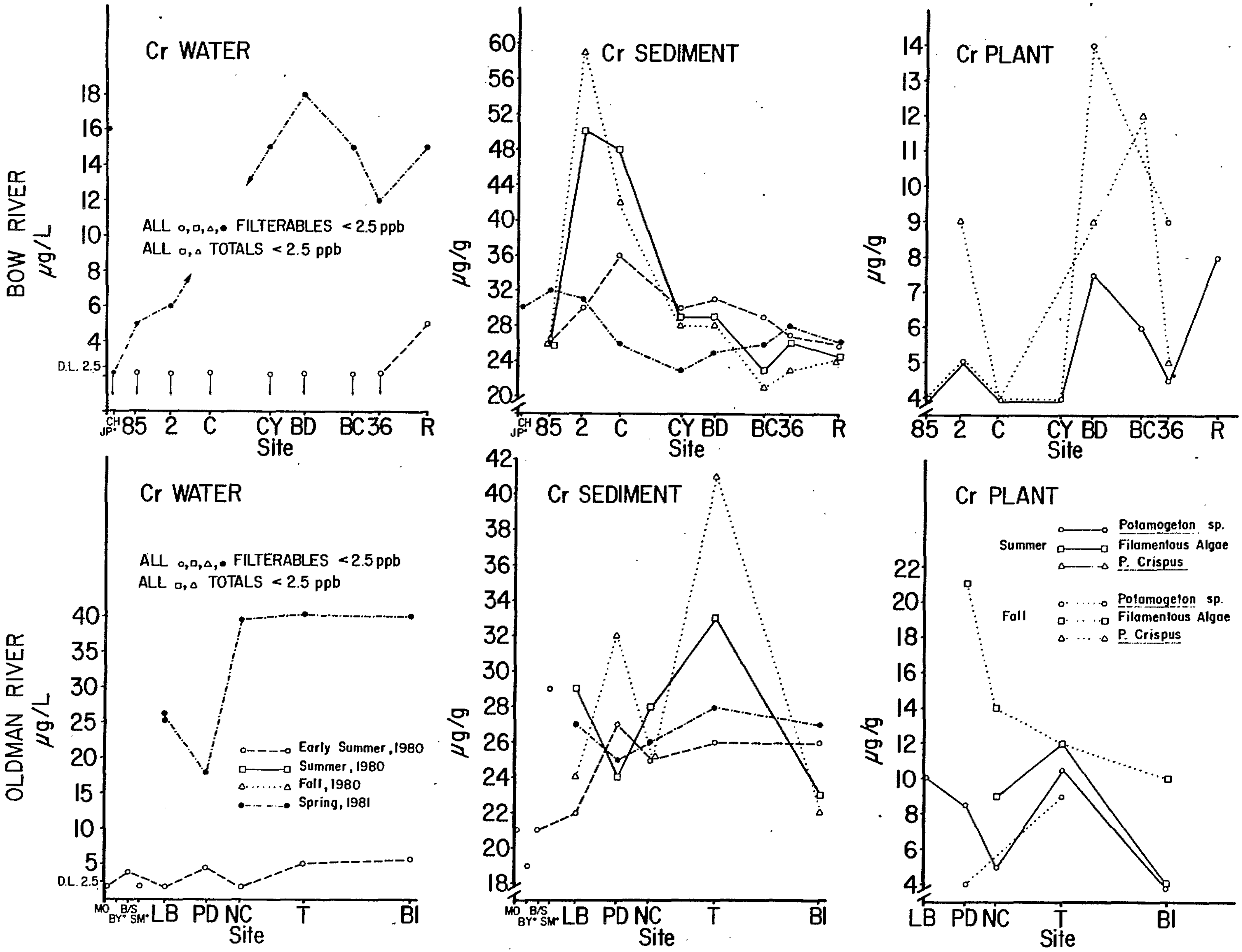

Figure 21. Chromium concentrations in water, suspended sediment and plant phases for the Bow and Oldman Rivers. Distance between sites on graphs is proportional to actual river distances.

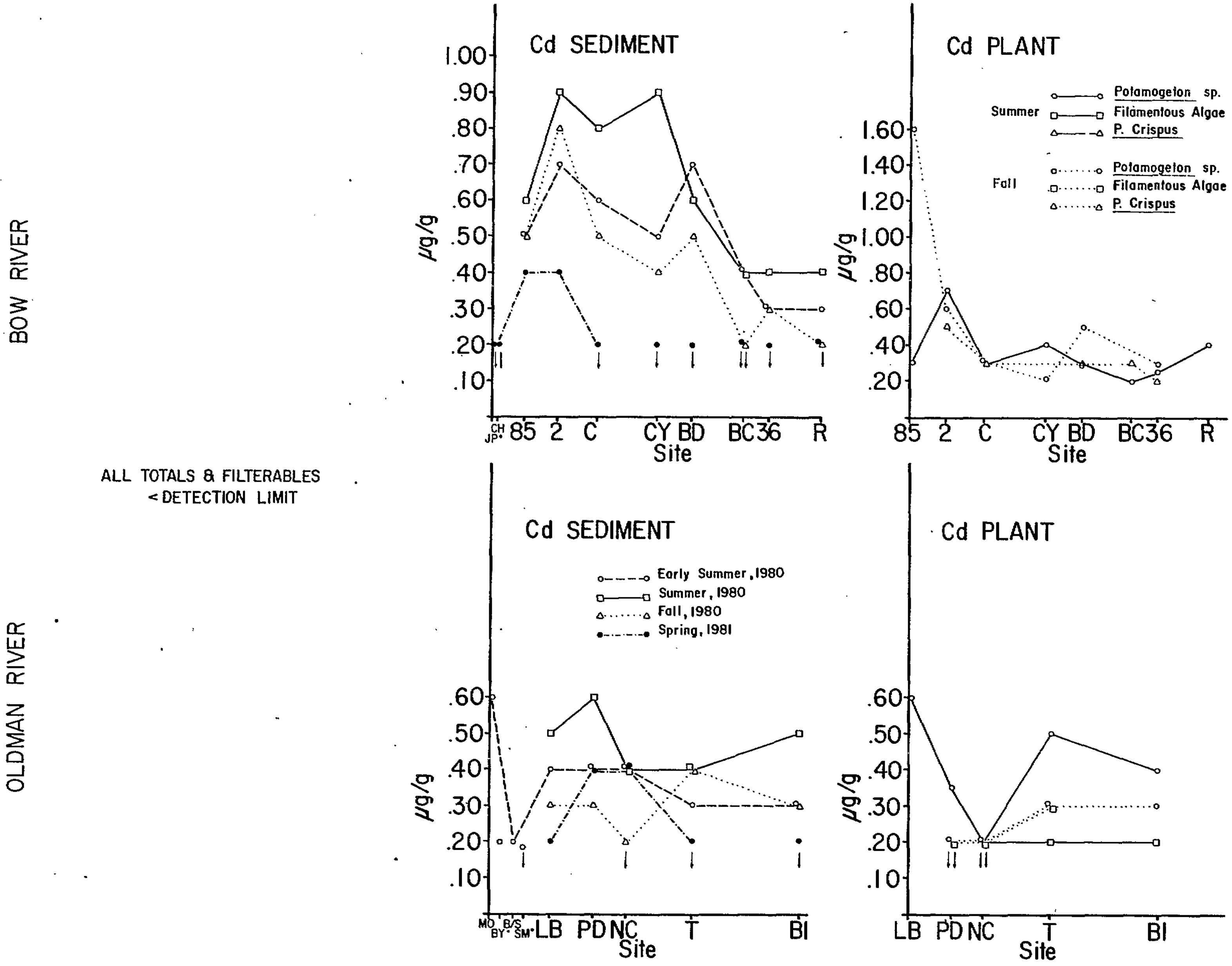

Figure 22. Cadmium concentrations in water, suspended sediment and plant phases for the Bow and Oldman Rivers. Distance between sites on graphs is proportional to actual river distances.

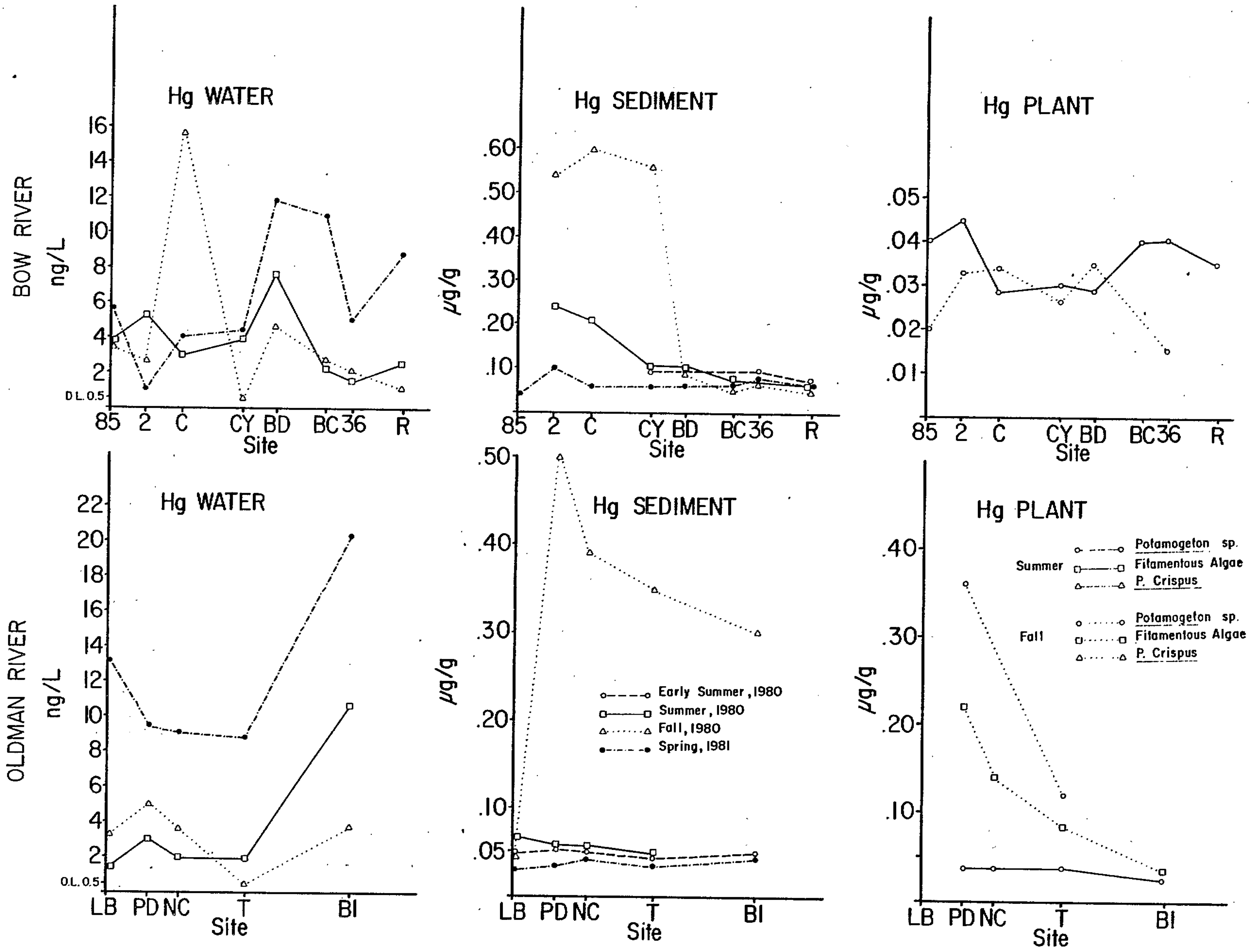

Figure 23. Mercury concentrations in water, suspended sediment and plant phases for the Bow and Oldman Rivers. Distance between sites on graphs is proportional to actual river distances.

to BRR. The high Total Zn at BR85 is an anomaly.

Although sediment-related metal is generally at background (see below), the large quantity of sediment in a Total sample produces elevated concentrations of individual metals in a water sample. Total metals values in spring, therefore, reflect diffuse sources of eroding sediment from foothills and prairie surfaces.

Total Pb, Co & Cd are not detectable in spring water. These elements are also present in distinctly lower concentrations than the other metals in background (bank) materials (Table 6). Filterable Mn & Cu are marginally above detection and have no trends. Filterable Zn values are disregarded here due to contamination of the filtered samples.

Early summer, summer and fall concentrations are detectable for total Mn, Fe, Cu and Zn. Total Cr is only detectable in early summer. Total Hg was not sampled in early summer but was found in detectable concentrations in both summer and fall. Filterable concentrations of all metals except Mn and Cu are below detection limits. Total metal concentration in ealy summer, summer and fall are all low and show only minor trends. Iron, Mn & Cu are marginally higher in early summer than in summer or fall, probably a reflection of a somewhat higher suspended sediment concentration at that time of year. For all metals, concentrations are lowest in the fall, the period of least sediment transport on the Bow River.

An early summer trend in Total Mn, Fe, Cu and Zn is evident. Values gradually increase from BR85 to BRCY, drop at BRBD then increase to a peak at BRR. This trend is similar to that of sediment concentration (peaks at BRCY and BRR).

The only trends in summer are an increase in Fe and Zn from BR85 to BRCY and from BR85 to BRBD for Mn and Hg; both then decline downstream without any apparent association with suspended sediment concentration. The fall peak of Total Cu at BR36 presumably reflects the presence of Cu-enriched diatoms (Akena, 1979).

Bow River: Suspended Sediment

Metal concentrations associated with suspended sediments in the Bow River reflect seasonal concentrations of solids, various sources of contamination, sediment inputs, and localized changes in organic content and particle size. Most of the metals are at an annual minimum concentration on sediments in the spring and reach a maximum during summer and fall. Early summer sediments show variable concentrations of metals relative to the other seasons.

The metals Mn, Ni, Cu, Pb, Zn, Cr, Cd & Hg are essentially at background levels in the spring. Diffuse source runoff/erosion and bank slumping contribute large quantities of solids to the river which reflect background chemistry of the surficial geology of the region. In the lower reaches of the Bow (BRBD to BRR) metal concentrations show little variation and are only marginally higher than in bank material in the same reach. For example, average concentrations of Fe, Mn, Pb, Cd & Hg found at BRBD and BRBC (1.95% and 396, 16, <0.2 & 0.016 mg/kg, respectively) compare closely with levels in bank material of 1.70% and 310, 07, <0.2 & 0.034 mg/kg (Table 6). Metals levels at background river sites (e.g. CH, BR85) have similar values.

TABLE 6: Metal Concentrations in Bank Materials.

mg/kg	ORPD		ORBI	BRDB	BRBC	
Cu	19	20~	10	13	13	12~
Pb	13	15	10	7	8	7
Zn	65	68	51	48	61	60
Co	7	7	5	7	6	6
Ni	19	23	18	19	19	20
Mn	218	209	262	266	327	338
Cr	25	22	22	27	21	19
Fe %	1.96	1.76	1.66	1.81	1.66	1.62
Cd	<.2	<.2	<.2	<.2	<.2	<.2
Hg	.061		.040	.027	.040	

~ duplicate analyses

During periods of snowmelt, especially when coupled with regional rainfall, the concentration of sediment-related metals is largely determined by natural inputs of sediment having background levels. In the early summer, summer and fall, metals concentrations on suspended matter appear to be directly influenced by contaminant inputs from Calgary and from tributaries.

The concentrations of Pb, Cu, Cd and Ni in early summer increase from BR85 to BR2, fall off to BRCY, increase to a lesser degree at BRBD, then decline downstream. The increase at BR2 is a direct response to inputs of metals from the Calgary area. The enriched sediments show a decline in concentration downstream where impoverished sediment inputs from the Elbow, Highwood Rivers (entering the Bow between BR2 and BRC) and from Arrowwood Creek (entering between BRC & BRCY) dilute the Bow River sediments. The increases in sediment concentration at BRC and BRCY (Figure 8) support this interpretation. The downstream trend in metal concentrations in the spring shows a lesser peak at BR2, followed by a rapid reduction to baseline levels that coincides with a ten-fold increase in sediment concentration. The reduced peak at BR2 reflects the greater sediment concentration during the spring runoff period; this serves to reduce the impact of contaminants from Calgary on a unit weight basis of suspended matter.

The early summer increase in Pb, Cd, Ni, Zn and Cr at BRBD (noted above) may reflect mobilization of metals from bottom sediments of Bassano Reservoir. The release of metals to the water phase and their subsequent adsorption to, or coprecipitation with suspended matter during reaeration in transport over the dam may be responsible for this observed trend. In addition, the increase may be accounted for by a slightly higher proportion of clay-size particles resuspended from the reservoir.

The early summer decline in metal concentration downstream from BRBD is due to increases in sediment concentration. These data suggest that dilution by impoverished mineral material from bank collapse and minor tributary sources is occurring.

The early summer peaks of Zn & Cr occur at BRC (rather than BR2 as for the suite of metals noted above). This disjointed peak may be related to the time and/or conditions required for Zn and Cr in solution to precipitate or adsorb to suspended matter.

Summer concentrations are higher than those in spring and early summer for Mn, Cu, Pb, Zn, Cr, Co, Cd & Hg. Although organic content also rises in the summer, the elevated sediment-metals concentrations undoubtedly reflect a low concentration of suspended matter in the river and, therefore, a greater impact at Calgary per unit weight of sediment.

Downstream trends of Zn & Cr are identical to those described for early summer levels of Pb, Cu, Cd & Ni. The reduced sediment inputs from tributaries are still effective in diluting the high metal concentrations associated with BR2 suspended sediments and, although mineral inputs from bank slumping are reduced, material is added in sufficient quantity to effectively lower concentrations to those found at BRBD. Cobalt trends are similar in the upper reaches of the Bow but show a minor decline at BRBD. The high Cu concentration at BR85 is an anomaly. Cadmium shows a second peak at BRCY (as opposed to BRBD). Concentrations of Pb & Hg decline from BR2 to BRR.

Fall concentrations are below those of summer for most metals with the exception of Cu & Hg. The peak value (BR2) of Cr is higher than that of summer; concentrations show a more rapid decline from this peak than do summer values.

Downstream changes in concentrations in fall are similar to early summer and summer trends (peak at BR2 and BRBD with subsequent declines) in the cases of Zn, Cr & Cd. Lead declines steadily from BR2 to BRR, as in the summer. This suggests that Pb is not being mobilized from Bassano Dam sediments in measureable quantity during summer or fall. Concentrations of Co are lower in fall than in any other season and show no trend. The fall trend in Cu concentration and sediment organic content are very similar with elevated levels at BR2 and BR36. Copper is known to be associated with organic matter. The organic peak at BR2 was caused by excessive collection of large pieces of organic debris prior to a change in centrifuge collection procedure at this site to eliminate this effect.

Concentrations of Hg decline sharply from BRCY to BRBD. The possibility of Hg being released from the sediments of Bassano Reservoir is supported by an increase in Total-Hg in the water phase.

This also occurs in early summer and summer; however, in no season is a corresponding increase in sediment-Hg observed.

Sediment-Mn, Ni & Fe show unique relative seasonal concentrations and downstream trends. Manganese peaks in each season at BR85, decreases to a low level at BRC, then gradually increases downstream to (spring) or higher (fall) background concentrations. Iron is highest in spring and early summer; trends in early summer and summer are similar (decreases at BR2, BRCY & BR36 with an overall downstream increase in concentration). Iron declines from BRC to BRBD in spring whereas the BRBD value is a peak in the fall trend. Nickel shows no similarity between seasons other than elevated values at BRBD in spring, early summer and fall. Decreasing concentrations of Mn at BRC and Fe at BR2 may be due to the introduction of contaminants and organic solids from Calgary sources diluting the mineral component of the suspended solids. Interpretation of Mn, Ni and Fe requires biogeochemical information beyond the scope of this study.

Bow River: Aquatic Plants

Aquatic macrophytes found in greatest abundance in the Bow River over the 1980 growing season were *Potamogeton* sp.. *P.vaginatus* accounted for most of the biomass downstream from Calgary. *P.filiformis* and *P.crispus* were also observed at many but not all sites. Because of difficulties in identification (due to hybridization and morphological similarity at various growth stages) and because the various species were frequently found growing entwined with each other, the macrophyte samples were often a composite of species and were identified only to the genus level. *P.crispus* was collected separately as it was more readily identified. The potamogeton species sampled absorb nutrients through the roots and submerged leaves. As noted above, the very coarse-grained substrate, while creating an adequate rooting environment, provides little sediment-related nutrition for root uptake. Nutritional uptake through roots probably reflects mainly soluble materials in river water as they pass through the coarse substrate under hydraulic forces. Concentrations of metals in plants, therefore, should reflect availability of metals in the water phase rather than a reservoir of labile material in bottom sediments.

Accumulation of most metals (Ni, Fe, Cr, Pb, Zn, Cu & Cd) is greater in fall plant samples than in summer. Only Mn, Co & Hg are present in higher concentrations or show higher peaks during the summer. The presence of epiphytes, the abundance of filamentous algae growing amongst the macrophytes in the fall, and the association of entrapped fine-grained mineral sediment by the plants contribute to elevated fall concentrations.

The concentration of metals associated with plant material is significantly lower than on sediments for Ni, Fe, Cu, Pb, Cr & Hg. For each of these metals, the concentration is approximately five-fold greater on suspended sediments (comparing all sites in summer and fall). Only Co & Cd shower higher peak concentrations in plants than on sediments. Manganese and Zn are lower than levels on suspended sediment but are of similar magnitude.

The trends in summer and fall concentrations of Cu, Pb, Zn, Cr & Cd are similar. All plants show concentration increases at BR2 and BRBD, with rapid declines downstream from these sites to background (=BR85) or below background. Summer peak levels of Zn, Pb & Cd occur at BR2 while peaks of Cu & Cr occur at BRBD. In the fall, Zn reaches a maximum value at BR2 while Cu, Pb, Cr & Cd peak at BRBD. The above suggests that, over the growing season, Zn is more accessible to macrophytes at BR2 (source of contaminants in solution) and that Cu & Cr are more readily available at BRBD (locations of metal release from sediments). The BR85 Cd concentration would appear to be an anomaly.

The trend of summer Co shows a BR2 peak and an immediate return to BR85 values. The fall peak is minor. Mercury rises slightly at BR2 and then again at BRBC. The decline froom BR2 to less than the BR85 value suggests that the latter is not a realistic background concentration. The failure to find an increase at BRBD in summer despite an increase in Hg in water, indicates that the water-related Hg is not available at that site. In the fall, a similar situation exists at BRC.

Summer trends of Mn, Ni & Fe decrease from BR85 to BR2 or BRC then increase downstream to BRR. These trends do not resemble those for detectable Total metal in water.

Differences in metal concentrations associated wth P.crispus and Potamogeton sp. (not including P.crispus) are not evident.

Oldman River: Water

It has been noted above that seasonal concentrations of metals in water are attributable to differences in sediment concentration and particle-size characteristics. Spring metal concentrations in water are distinctly higher in spring in the Oldman River than in other seasons. Total metals are lower in early summer and, where detectable, very low and of similar magnitude in summer and fall. Cadmium was not detectable in water in any season. The high spring values reflect, as in the Bow, the high concentrations of suspended sediment carried downstream during spring runoff. These sediments are fine-grained (Figure 8), and have low organic content (Figure 9); their metal chemistry (as noted below) is essentially background.

In early summer suspended sediment concentrations, while still reflecting prairie runoff, are an order of magnitude lower than in spring. Although suspended sediment is more enriched in early summer than in spring (see below) metal concentrations in water are lower because of the large reduction in the suspended sediment contribution to a "Total" water sample. A further reduction in suspended sediment concentrations is largely responsible for the reduction in Total metal values from early summer to summer and fall.

Filterable concentrations are detectable in all seasons for Cu and Mn. Nickel is detectable at only one site in early summer and fall whereas Fe is detectable at one site in spring and fall. Contamination of samples obviates any use of filterable Zn data.

Spring concentrations of Total Mn, Ni, Fe, Cu, Zn & Co show a progressive increase from LB to ORBI due to increasing suspended sediment concentratons and a proportional increase in clay-size material. Lead and Cr respectively peak and decline at ORPD, then increase downstream. These are the only two metals which parallel observed trends of sediment-associated metal, an observation which is explained by the close relationship between these two metals and solid matter (Forstner, 1977). Mercury declines from LB to ORT, but peaks at ORBI. There appears to be a source of soluble Hg in the ORBI reach which causes Total Hg to peak here in all seasons. Sediment-associated Hg does not show this trend.

In **early summer** Total Mn, Fe, Cu & Cr increase from LB to ORPD and a downstream increase from ORNC. The ORPD peak results from the rise in suspended sediment concentration at this site plus the impact of Lethbridge. The subsequent downstream increase in Mn, Fe & Cr appears to reflect changes in solids-related metal concentrations. Nickel, Pb & Zn show large increases at ORT, suggesting a source of these elements in the vicinity of this site. Notably, filterable Ni was also observed at this site.

Manganese, Fe, Cu, Zn and Hg were detectable in **summer and fall** water. The trends of Mn and Fe (summer and fall) and Cu (fall) appear to reflect suspended sediment concentrations. Total zinc is marginally above detection and has no distinct trend. Total Hg peaks at ORPD and ORBI, likely reflecting inputs from Lethbridge and a source of soluble Hg (noted above) upstream from ORBI.

Oldman River: Suspended Sediment

Seasonal changes in sediment-associated metal concentrations reflect changes in suspended sediment concentrations, the impact of point sources, and organic content and particle size. Concentration of metals on sediment in **spring** are at background (same range as found in bank materials collected at ORPD and ORBI (Table 6), and in sediment from irrigation return flows). Manganese, Fe and Zn appear to be slightly enriched. Levels of Mn, Cu, Pb, Zn, Cr & Hg are highest in **summer** and **fall** in response to increased organic content and a severe reduction in the amount of sediment having only background chemistry.

Metal concentrations in the spring show minimal downstream variation. Trends in **early summer** parallel spring data for for Mn, Fe, Pb, Hg, and show enrichment below Lethbridge for Ni, Zn, Cr and Co, plus the effect of tributary sediment inputs.

Summer and fall trends clearly show the impact of Lethbridge and an unidentified source in the Taber area. Suspended sediment is enriched because of low sediment concentrations (reduced material having background chemistry) and a relatively higher organic content (especially in summer, Figure 9). Metals are at a summer maximum at ORT for Ni, Fe, Zn, Cr and Co while Cd peaks at ORPD. The high Mn value at ORNC is an anomaly. The elevated levels of Cu, Pb, Zn, Co and Cr at LB may result from urban storm runoff which was observed on numerous occasions during the summer sampling period.

The impacts noted at ORPD and ORT are also encountered in the fall for Mn, Ni, Fe, Cu, Pb, Zn and Cr. Of these metals only Cu and Pb are in greater concentration at ORPD than at ORT. All metals, except for Mn, deline rapidly in concentration downstream of the point source to at least "background" (LB) concentrations. Cobalt and Cd decline from LB to ORNC, suggesting sources of these elements upstream from LB. Cobalt and Cd increase again at ORT. The concentration of sediment-Hg increases ten-fold from LB to ORPD then declines downstream.

Oldman River: Aquatic Plants

Potamogeton sp. were collected at all sites on the Oldman in the summer, and at ORPD and ORT in the fall. Filamentous algae were collected at ORNC, ORT and ORBI. Plants were not observed in the LB reach in the fall. Algae was found at all downstream sites whereas Potamogeton sp. were only observed at ORPD and ORT. Luxuriant aquatic plant growth was observed on the Oldman River only at ORPD in both summer and fall seasons, and at ORBI in the fall.

Metal concentrations in plant materials are higher in the fall than in summer for Mn, Ni, Fe, Cu, Pb, Zn and Cr. In each case greater concentrations occur in the filamentous algae. In contrast, mercury is more concentrated in fall macrophytes than in algae, whereas Cd is higher in summer in macrophytes. In comparison with suspended sediment-associated metal concentrations, plant metal levels are appoximately one-third for Ni, Fe, Cu, Pb, Zn and Cr. Cadmium and Hg are concentrated to about the same extent by each of the plant and sediment phases.

Downstream trends in metal concentrations are similar for Potamogeton sp. and filamentous algae. The exception is Cr, for which the species trends differ in the fall. Lead and Mn in macrophytes show only minor peaks at ORT that are not reflected in algae. Significant summer peaks in Ni, Fe, Cu, Zn, Cr and Cd are found at ORT. In each case the peak is followed by a sharp downstream decline.

The high concentration of metals at LB in the summer is probably unrealistic, reflecting the micro-environment of the plant sampled in this impoverished reach (plant was located mid-stream in a sheltered sedimentary location and was senescent).

Fall trends show peaks at ORNC for Mn, Ni, Fe, Cu and Zn, at at ORPD for Cr and Hg. Cadmium and Pb increase at ORT. The peaks at ORNC are not mirrored in sediment-associated metals nor in water samples (Total/Filterable).

ORGANOCHLORINE RESIDUES

Our work, in part, was to establish pathways and characteristic distributions of a suite of nonionic pesticides, PCB and chlorobenzenes amongst the water, suspended sediment and plant phases (Ongley & Blachford, 1982). Pesticides and PCB residues characteristically have low solubility, high adsorptivity and are persistent. The chlorobenzenes are relatively soluble and volatilize more readily. Adsorption of organochlorine residues onto solids is a common mechanism by which they are removed from the aquatic medium (Hague et al.,1977) and transported in the fluvial environment (Pionke, 1977). Studies have indicated an average of 61% of DDT and 15% of dieldrin in bulk water samples are associated with sediment (Miles, 1977). The adsorption potential of a residue increases with the number of chlorine atoms in the molecule (Hague et al., 1977) and is affected by temperature and by the surface area and organic content of the adsorbant. DDT, dieldrin and PCB are known to be adsorbed from aqueous solutions by particulate matter in direct relation to the organic content of the material (Hague et al.,1977; Weber, 1972). This is thought to be due to the high surface area and the various functional groups of the organic matter. Pesticide adsorptivity may be 10 to 1000 times greater on organic matter than on mineral solids (Pionke, 1977).

Determination of phase distributions and downstream trends were limited by the low to nil presence of many of the organic residues. A number of the pesticides (eg. DDT) have been delisted for some years and are now found in the environment in small residual amounts.

The minimum detectable concentration is 0.01 ppb for all residues in water and for sediment and plant chlorobenzene residues, and 0.01 ppm for sediment and plant organochlorine and PCB residues. Although the samples were scanned for all common organochlorine pesticide residues including α, β and γ-HCH, α, γ and oxy-chlordane, aldrin, endrin, dieldrin, heptachlor, HE, methoxychlor, DDT and its metabolites, plus mirex, photomirex, and PCB, only those residues which were found in at least one of the sediment, plant or water phases are reported here. Also, because most of the detectable residues are at, or close to minimum detectable levels, the results (Figure 24) are expressed as the percent of samples from both rivers (for similar seasons) having detectable residues.

The residues preferentially associate with one or more of the sediment, plant or water phases. The phase distributions are affected by the solubilities and distribution adsorpton constants of the residues, the association with and potential for uptake by aquatic vegetation, and the hydrologic characteristics of the sampled fluvial regimes.

Solubility of the organochlorine residues range from 0.001 ppm (Weber, 1972) for DDT to 637 ppm (Hague et al., 1977) for one of the PCB isomers. An increased degree of chlorination decreases the solubilities of the coumpounds. Except for γ-HCH (which was not present in our samples) the chlorinated hydrocarbon insecticides and PCB's are considered insoluble in water (Weber, 1972). This is evident in their absence in the water phase in each season. DDE is present in water in the fall, presumably reflecting the more favourable conditions for decomposition of DDT and its greater solubility than its parent compound. The more soluble chlorobenzenes are present in significant frequencies in the water phase in summer and fall; their absence in water and solids in the spring presumably reflects a dilution by large volumes of water and of suspended sediment having background chemistry (as for phosphorus and metals) and which reduces any chlorobenzenes to levels below detection. Volatile losses are known to occur from aqueous systems for DDT and to a lesser extent for dieldrin, chlordane and HCH (Weber, 1972). The magnitude of loss of these compounds from these fluvial systems cannot be assessed by the design of the present project.

As for many of the metals, the data indicate a greater amount of sediment-associated residues in the summer and fall (when suspended matter was distinctly higher in organic content) than in the spring (when the suspended load is dominated by mineral sediment). The lower spring values may reflect dilution by the higher discharge and sediment concentrations.

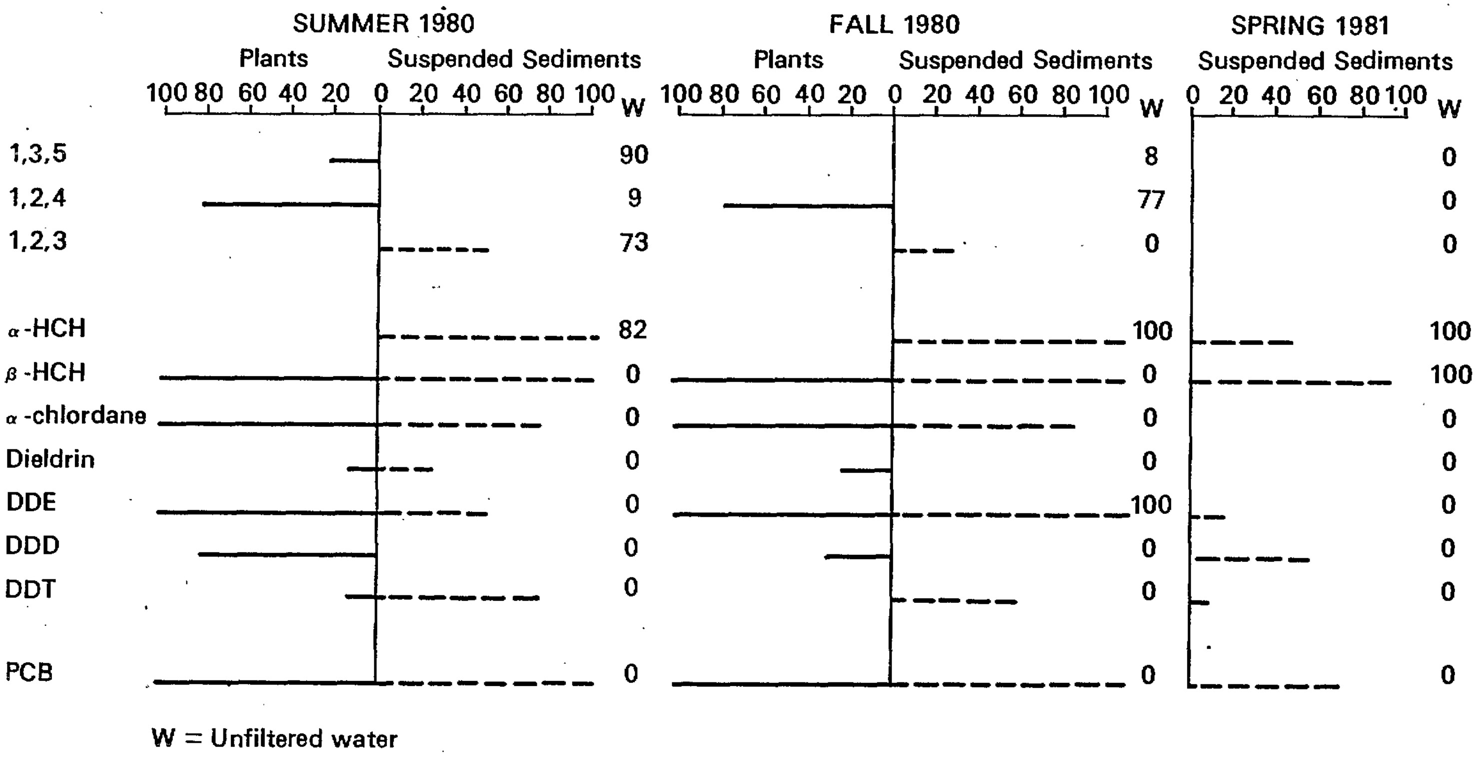

Figure 24. Seasonal phase distributions of chlorobenzenes, organochlorines and PCB for the Bow and Oldman Rivers. The values for plants, suspended sediments and water samples(W) indicate the percentage of samples in which detectable quantities of the substance were found. Plant matter was not sufficiently available in the spring.

Association of the residues with the plant phase may occur for the soluble compounds by means of absorption and, for the relatively less soluble compounds, by adsorption on the outer vegetative surfaces (Cope, 1965) and/or entrapment by the plants of sediment-associated contaminants. β-HCH, γ-chlordane and DDE indicate equal or greater accumulation in the plant than in the sediment phase, therefore both mechanisms are likely in operation. The rapid conversion of DDT to DDE may be responsible for the absence of the intermediate form DDD in the sediment. DDD is, however, found in plant material. It is not clear whether this is due to impaired ability to detect DDD in sediments diluted by sediment additions during downstream transport, an intrinsic association of DDD with plant matter, or differing rates of DDT decomposition in sediment and plants. The increasing frequencies of successive metabolites of DDT in plants suggest that degradation is occurring with accumulation of metabolites through time. The soluble 1,3,5 and 1,2,4 chlorobenzene isomers are likely absorbed by plants from the water phase during the growing season.

The solubilities of the compounds are inversely related to the tendency to adsorb to solids. Distribution adsorption constants (Kd) are experimentally determined values that express the partitioning of a compound between sediment and water phases. Values are not available for many of the residues considered here. Field-derived Kd values are essentially what are expressed in Figure 24, with the inclusion of the plant phase.

The trends that are evident are in the trichlorobenzenes in water, 1,2,4-trichlorobenzene and PCB in plants, and 1,2,3 trichlorobenzene, β-HCH, p-p'-DDT and PCB in suspended sediments. Generally, Bow River water shows concentration peaks at BR85 (possibly from an upstream source or from urban diffuse runoff), BRC (possibly contributed by the Highwood River), BRBD (release from the bottom sediments of the reservoir), and BRR. On the Oldman River all the water values are constant. Bow River plants have declining concentrations of the 1,2,4 isomer and PCB from BR2 to BRBD. The only trend in the Oldman River plants is an increase from ORT to ORBI. Bow River suspended sediments show rapid concentration declines from BR2 or BRC to BRBD (for the 1,2,3 isomer, β-HCH and p-p'-DDT) and increases of PCB at BRBD. Sediments in the Oldman have declining concentrations of the 1,2,3 isomer and p-p′-DDT from ORPD to the mouth (ORBI) and of PCB from LB downstream.

LOADINGS SCENARIOS: BOW AND OLDMAN RIVERS

Loadings of heavy metals and phosphorus give an indication of the cumulative impact of these two rivers on the mainstem of the South Saskatchewan River. Loadings are calculated with data collected at the most downstream site (BRR & ORBI) on each river. Biomass load (for the Bow River) represents the cumulative load stored in biomass (macrophytes) for the entire length of river from Calgary to BRR. Because of the time-variant and discharge-dependent nature of loadings of sediment-associated substances, loadings calculated from one sampling run per season provide only a crude estimate of load (Ongley et al. 1977). This, however, at least allows some notion of comparative loadings amongst the various phases (plant, sediment, total). Biomass load, because it is the cumulative load for the river, implies an amount which would be transported downstream into the South Saskatchewan River if all aquatic biomass were up-rooted and transported downstream as organic mats without significant decay whilst en route. This is an assumption which will vary greatly depending on the particular hydrologic conditions which prevail in any particular year.

Loads in water (Table 7) were calculated over the six month period, May-October 1980, for which sampling was conducted. The period was divided into a high-water (May, June) and low-water (July-Oct.) sub-period by examination of the river hydrographs. An average of the concentrations of each variable sampled during each sub-period was assumed to represent the concentration of the variable for each month of the sub-period. The products of average concentration, monthly mean discharge and a time/conversion factor were summed for each month of the high and low-water sub-periods to yield a load (metric tonnes).

Loads of sediment-associated variables were calculated in a similar manner. The average sediment-associated concentration was multiplied by the suspended sediment concentration and discharge for each month and summed for the sub-period.

NOTE: Concentrations of some metals were below detection. For this

TABLE 7: Estimated Heavy Metal and Phosphorus Loads in the Bow and Oldman Rivers; May-October, 1980 (metric tonnes)

	TOTAL LOAD IN WATER AT BRR			LOAD ON SUSPENDED SEDIMENT AT BRR			STORAGE~ IN BIOMASS
	High Water	Low Water	Total	High Water	Low Water	Total	Total
Bow River: at BRR							
Pb	10.33*	5.23*	15.56*	4.86	0.260	5.12	42.6
Zn	5.27	1.41	6.68	19.14	0.363	19.50	338.
Cu	7.65	0.89	8.54	5.75	0.14	5.89	30.8
Ni	20.66*	2.62*	23.28*	4.96	0.098	5.06	46.9
Cr	9.92	1.31*	11.23*	4.66	0.11	4.77	23.5
Cd	1.03*	0.52*	1.56*	0.09*	0.0023*	0.101*	2.1
Co	5.17*	2.62*	7.78*	1.68	0.61	2.29	69.5
Mn	107.46	4.66	112.12	104.55	3.73	108.27	1522.
Fe	5584.9	156.47	5741.37	4305.10	78.37	4383.5	872.
Hg	8.99x10-3	9.78x10-4	9.97x10-3	1.29x10-2	1.6x10-4	1.3x10-2	0.132
P	247.99	32.44	280.43	223.19	52.68	275.86	13,581.
OLDMAN RIVER: at ORBI							
Pb	15.96*	2.64*	21.24*	10.67	0.02	10.69	
Zn	81.97	0.65	82.62	70.78	0.14	70.92	
Cu	22.12	0.29	22.41	21.69	1.43	23.12	
Ni	26.22	1.32*	27.54*	18.49	0.05	18.54	
Cr	26.45	0.66*	27.11*	18.85	0.05	18.89	
Cd	1.14*	0.26*	1.40*	0.36*	0.0008	0.36*	
Co	11.66*	1.32*	12.98*	6.76	0.02	6.77	
Mn	429.24	2.43	431.67	364.25	28.25	392.50	
Fe	20623.	98.49	20820.	16078.	478.50	16556.	
Hg	2.33x10-2	1.91x10-3	2.52x10-2	3.34x10-2	5.89x10-1	6.23x10-1	
P	345.78	6.86*	352.65*	622.49	10.81	633.29	

~ assumes 100% plant cover; Alberta Environment suggests this should be reduced by at least 25%.

* element not detectable; load assumes element has a concentration equal to detection limit; load is therefore maximized.

exercise, it was decided to assign the detection limit to the metal and calculate the load accordingly. Loads of these metals are, therefore, the maximum possible. The alternative, assuming a zero value for the metal and, consequently, a zero load was considered inappropriate for the purpose of developing loading scenarios.

Biomass load estimates (Table 7) are the product of average summer and fall concentration of each variable in plant tissue and the weight of biomass in each river reach. Macrophyte biomass estimates were provided by Alberta Environment for 1980, a period of significantly reduced biomass downstream from Bassano compared with 1979. The degree to which excessive growth might have reduced metal etc. concentrations at sites in the lower Bow because of uptake, is not known. In terms of total loadings for the six month period the presence or absence of biomass is probably not significant, mainly because of the control exerted (noted below) by suspended sediment. The biomass data were divided into reaches which correpond to the sampled sites. Biomass loadings assume 100% plant cover on the substrate of each reach; realistically, the load should be reduced by 25-50%.

The importance of suspended sediment concentrations to water chemistry during high water periods is also noted in the high-water loadings. For all metals, with the exception of mercury, the sediment-associated load comprises most if not virtually all of the Total load in water. The larger loads on the Oldman River reflect larger suspended suspended sediment concentrations rather than any substantial change in water chemistry. During low-flow periods both rivers have comparable suspended sediment concentrations; the larger discharge of the Bow produces larger loads in that river. Zinc loads on sediment are much larger than those of the water+sediment (ie.Total) component, and reflect sample contamination of that element.

For the entire six-month period our data suggest that loadings are dominated by high-water sediment flux. If these sediment-associated loads are largely unavailable (as suggested by speciation chemistry for irrigation-return flow sediments, noted below), the calculation of Total metal load would appear to be relatively meaningless for river management purposes unless it can be shown that these sediments will ultimately be deposited in a sedimentary environment which is conducive to metal release. It follows that the conventional practice of ascertaining Total metal concentration in a water sample is not especially meaningful in these rivers during periods of high flow unless that component which is associated with sediment is also determined. Unfortunately, the filtered component in spring and, for most metals, the Total component during summer are usually less than conventional detection limits. This presents something of a dilemma for most agencies unless they are willing to turn to much more rigorous analytical procedures.

Chemical loadings in biomass are generally greater, often very much greater than loadings in transit in the water column. These loadings represent a substantial component of the bio-available fraction which might reasonably be expected to be monitored in the water phase if there was no biomass below Calgary. Loadings in biomass, and especially that of phosphorus, represent a substantial reservoir of metals and nutrient which will be transported downstream during periods of storm flow and which never enter into conventional load estimates. The downstream significance of these large biomass loads lies in the fact that although these loads are accumulated over long reaches of river, the biomass will be transported during relatively short periods of time and will be deposited into a geographically restricted area (e.g. upstream end of a reservoir). It is not known what the fate of biomass transport is in the Bow River nor is it known to what extent plant-associated nutrient and metals are released back into the water column during decay once the organic material has been deposited. Our data suggest, for example, that there is leakage of metals from Bassano Dam sediments which, presumably, contain abundant organic detritus accumulated from the reach between Calgary and Bassano.

GEOCHEMISTRY OF IRRIGATION RETURN-FLOWS

Intensive agriculture in Southern Alberta is aided by large-scale irrigation organized into thirteen Irrigation Districts. These comprise some 400,000 hectares (one million acres). Irrigation return flows are the principal mechanism by which agricultural diffuse sources of pollutants are introduced to the Bow and Oldman Rivers. Although research has tended to focus on salt and sediment production from irrigated areas, this study focusses on sediment-associated phosphorus species, heavy metals and organochlorine residues.

Irrigation Districts have a major impact on the Bow and Oldman Rivers inasmuch as they divert significant quantities of water. Lethbridge Northern I.D., for example, diverts some 1.7×10^8 m^3 annually from the Oldman; the three irrigation districts on the Bow remove at least 1.2×10^9 m^3/year. Much of this water is returned to the Bow and Oldman Rivers as unconsumed water (not spread on land) or as runoff from irrigated surfaces via overland flow or, in more limited situations in southern Alberta, through tile drains.

Sampling in this study was restricted to four Irrigation Districts (Figure 25) which represent approximately 15% of irrigated land in Alberta. Sampling was carried out on seven return flows (three to the Oldman and four to the Bow) and one (Rolling Hills) distribution canal (Figure 1 and 25) at a sampling frequency of approximately two to three weeks from June to September. This represents the bulk of the irrigation period in 1980. Each site is represented by six samples. The sampling schedule and variables collected are outlined in Table 4. Because of large and unpredictable variability in discharge it was not possible to selectively sample from the range of discharges characteristic of return flows. Examples of return-flow hydrographs for each of the Bow and Oldman systems are presented in Figures 26 & 27 together with the position of the sampling times in relation to discharge. Sampling occurred over a range of discharge conditions representative of the irrigation season. The data represent, therefore, typical physical and geochemical characteristics of return-flow waters.

All sites were sampled for Total and Filterable metals. Five sites which had sufficient turbidity to enable five grams of suspended matter to be collected over a three hour period, were sampled for suspended sediment geochemistry. Although aquatic plants grow in some of the return flows, these were not sampled as it was assumed that significant flux of organic debris would not occur, mainly because the canals are emptied before plants become senescent. It is not known to what extent preceeding year's plant matter is flushed through these systems during the following spring flush-out.

Unfiltered (Total) water for organochlorine residue and mercury determination was collected twice, once in August and again in September (Table 4). Sampling and analytical procedures are those described elsewhere in this report.

Suspended Sediment Characteristics

The sampled irrigation return flows display two separate groupings in terms of suspended sediment concentrations (Table 8). One group has seasonal mean concentrations >100 mg/L (Piyami Drain, Little Bow River, and Expanse Coulee on the Oldman River, and Cairn Hill and New West Coulee on the Bow), while the second has seasonal mean concentrations which are only marginally above detection (Coal Creek, Twelve Mile Coulee and Rolling Hills).

Particle-size distribution is highly variable within and between sampled return flows (Figure 28). Only for Expanse and New West Coulees is there a substantial sand component at all times. The sampling site on Expanse Coulee is located on a relatively steep gradient between the upper prairie surface and the confluence with the Oldman River. This energy gradient is probably responsible for the large amount of sand transported through this system. Site conditions on New West Coulee do not reflect steep gradients but may be influenced by substrate and artificial straightening. With the exception of Rolling Hills Distribution Canal, organic content is generally less than 10% of the suspended sediment content, and usually less than 05%.

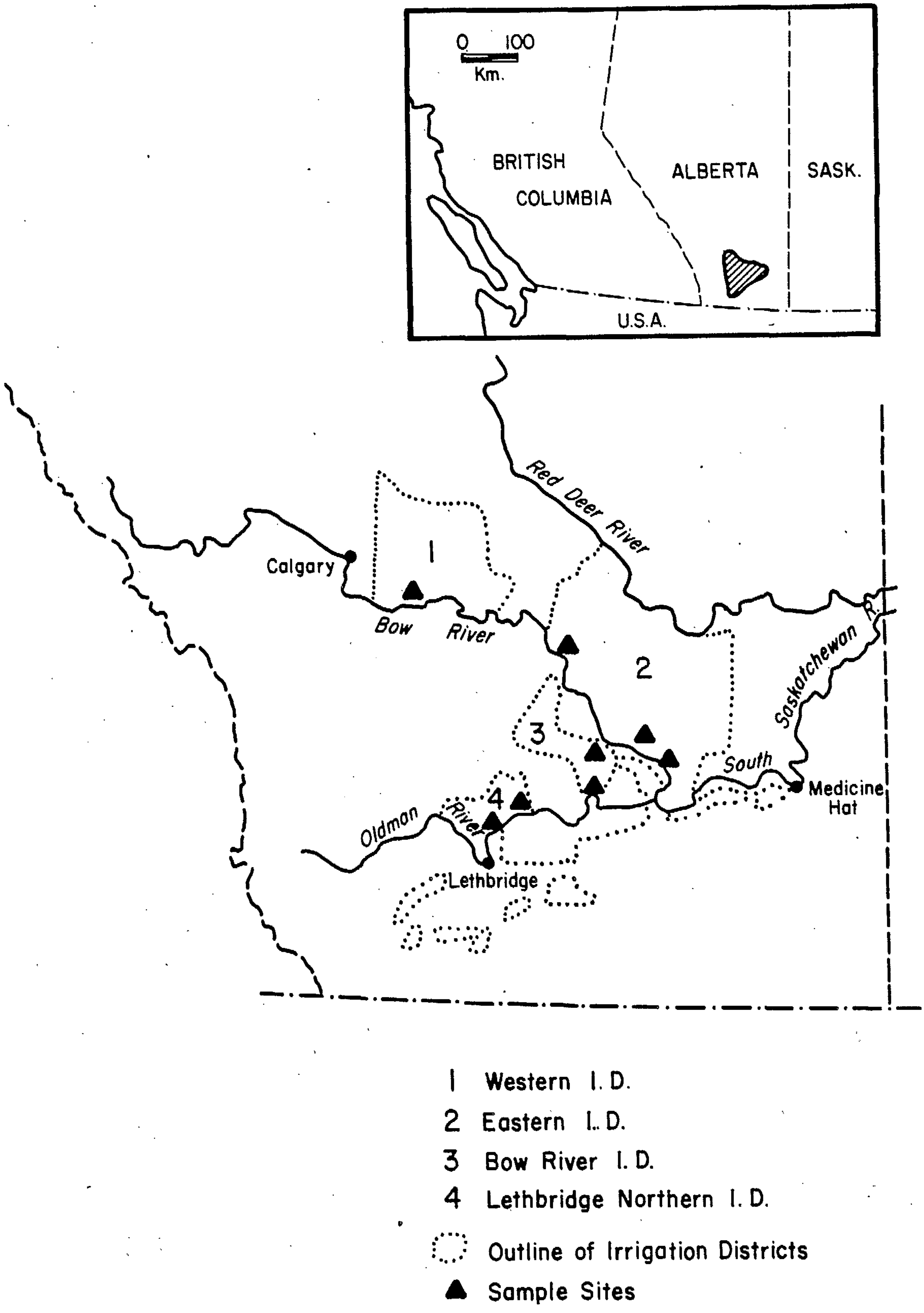

Figure 25. Irrigation Districts of Southern Alberta. Study sites are indicated.

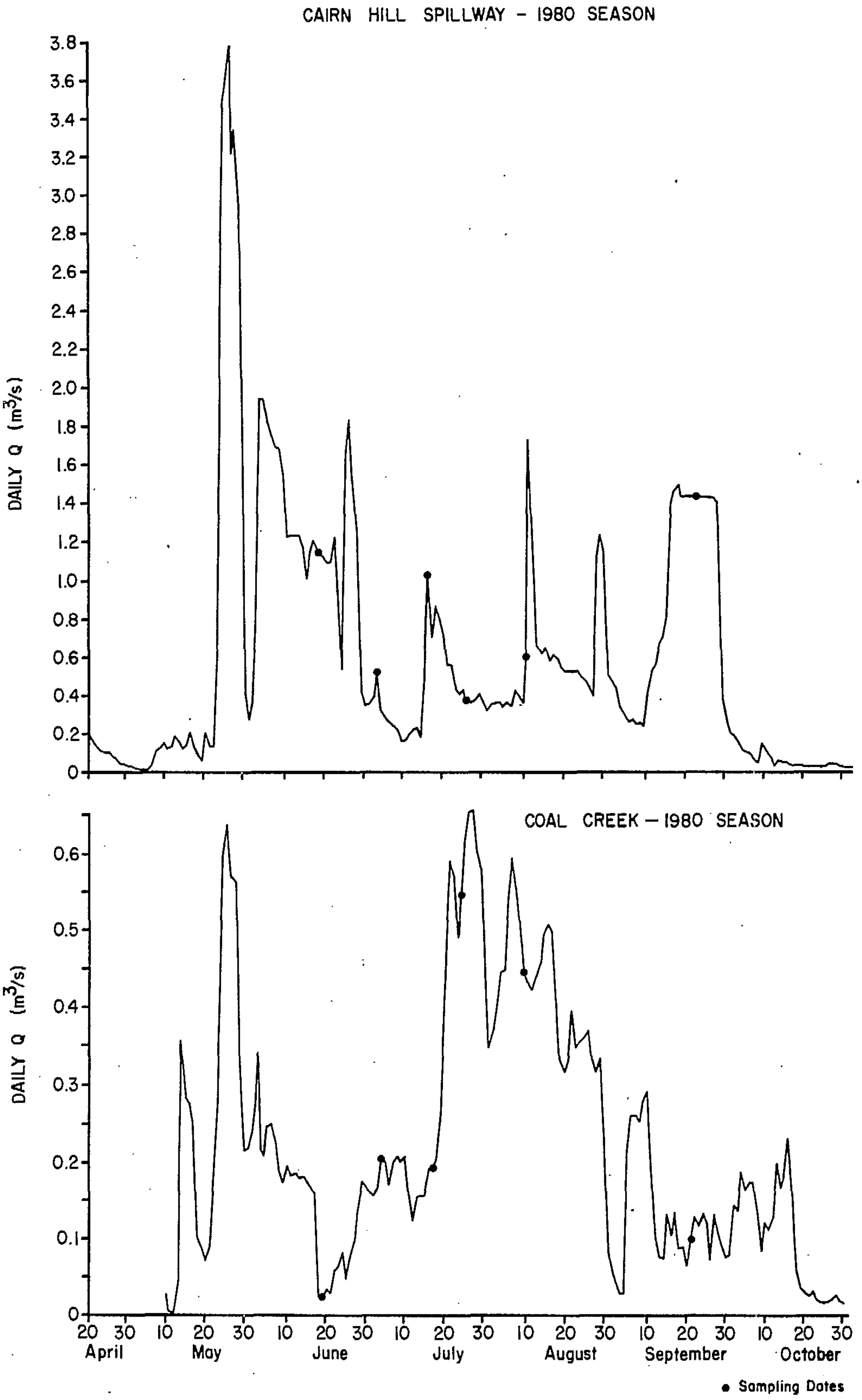

Figure 26. Irrigation return-flow hydrographs and sample dates for two sites tributary to the Bow River.

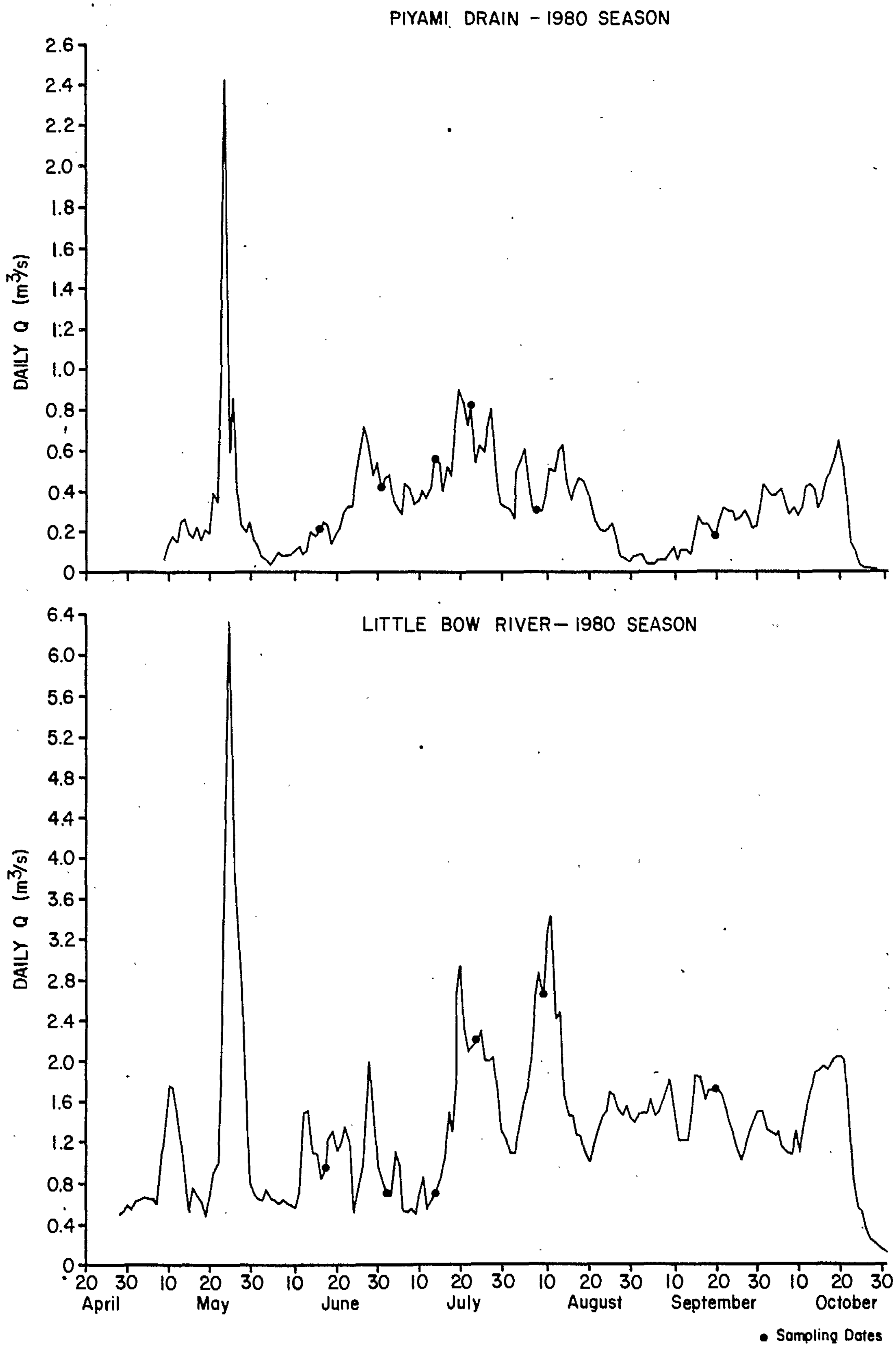

Figure 27. Irrigation return-flow hydrographs and sample dates for two sites tributary to the Oldman River.

TABLE 8. Mean Sediment-Associated Metals as Percent of Total (Unfiltered) Metals*

Site	Cu	Mn	Fe	Seasonal Average Suspended Solids Concentration (ppm)
<u>Oldman River System</u>				
Piyami Drain	67%	97%	99%	444.3
Little Bow River	17%	92%	99%	102.2
Expanse Coulee	18%	86%	99%	112.9
<u>Bow River System</u>				
Cairn Hill Spillway	33%	90%	96%	107.5
Coal Creek	37%	52%	74%	<10.
New West Coulee	43%	95%	99%	173.2
Twelve Mile Coulee	<1%	60%	85%	<10.
Rolling Hills D.C.	129%**	22%	14%	14.0

$$* \quad \frac{\text{Total} - \text{Filtered}}{\text{Total}} \times 100$$

** Values >100% occur when filtered metal values are greater than total metal values

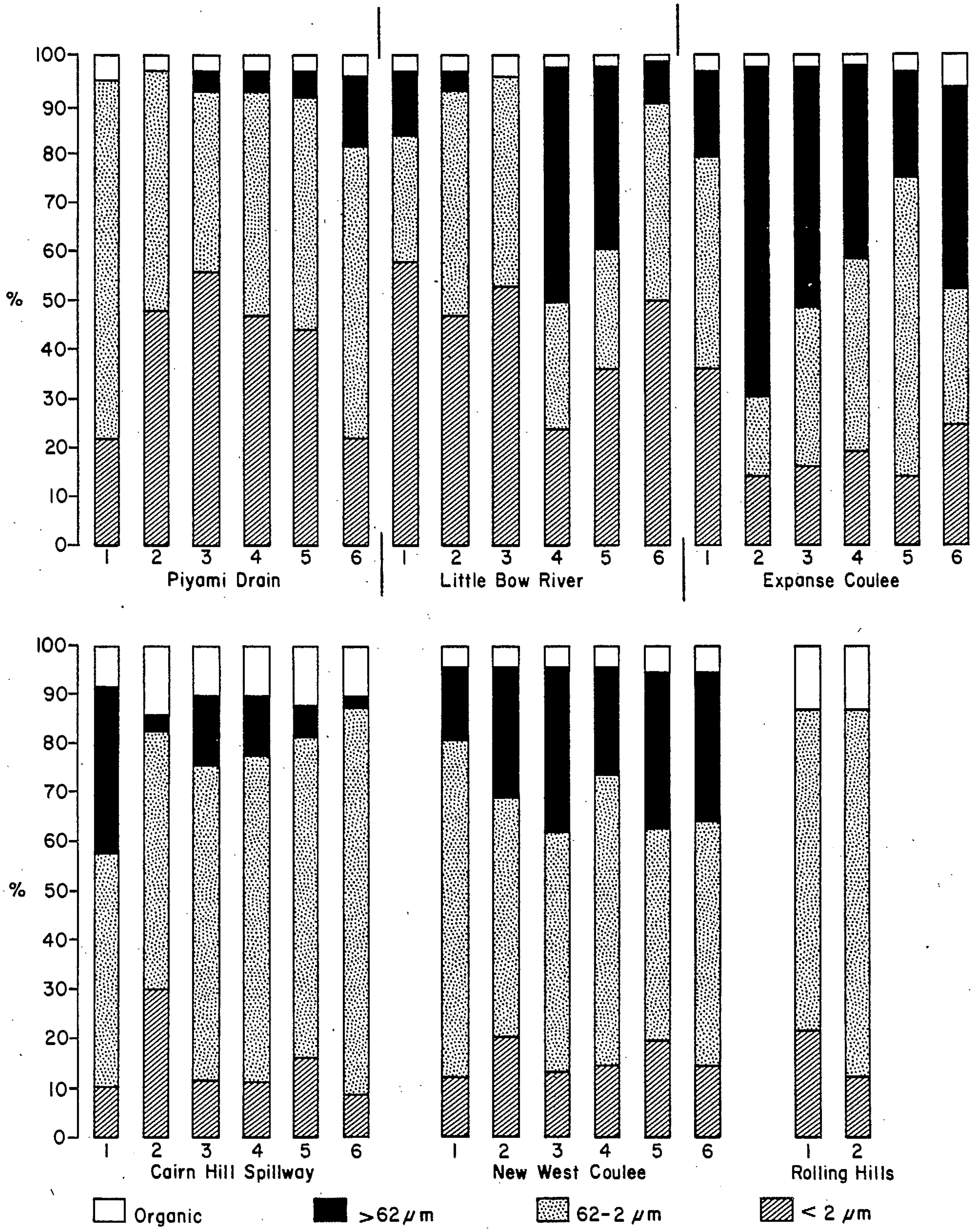

Figure 28. Particle-size distribution for suspended sediments in selected irrigation return-flows. Piyami, Little Bow and Expanse are tributary to the Oldman; Cairn Hill and New West are tributary to the Bow; Rolling Hills is a supply canal in Eastern Irrigation District.

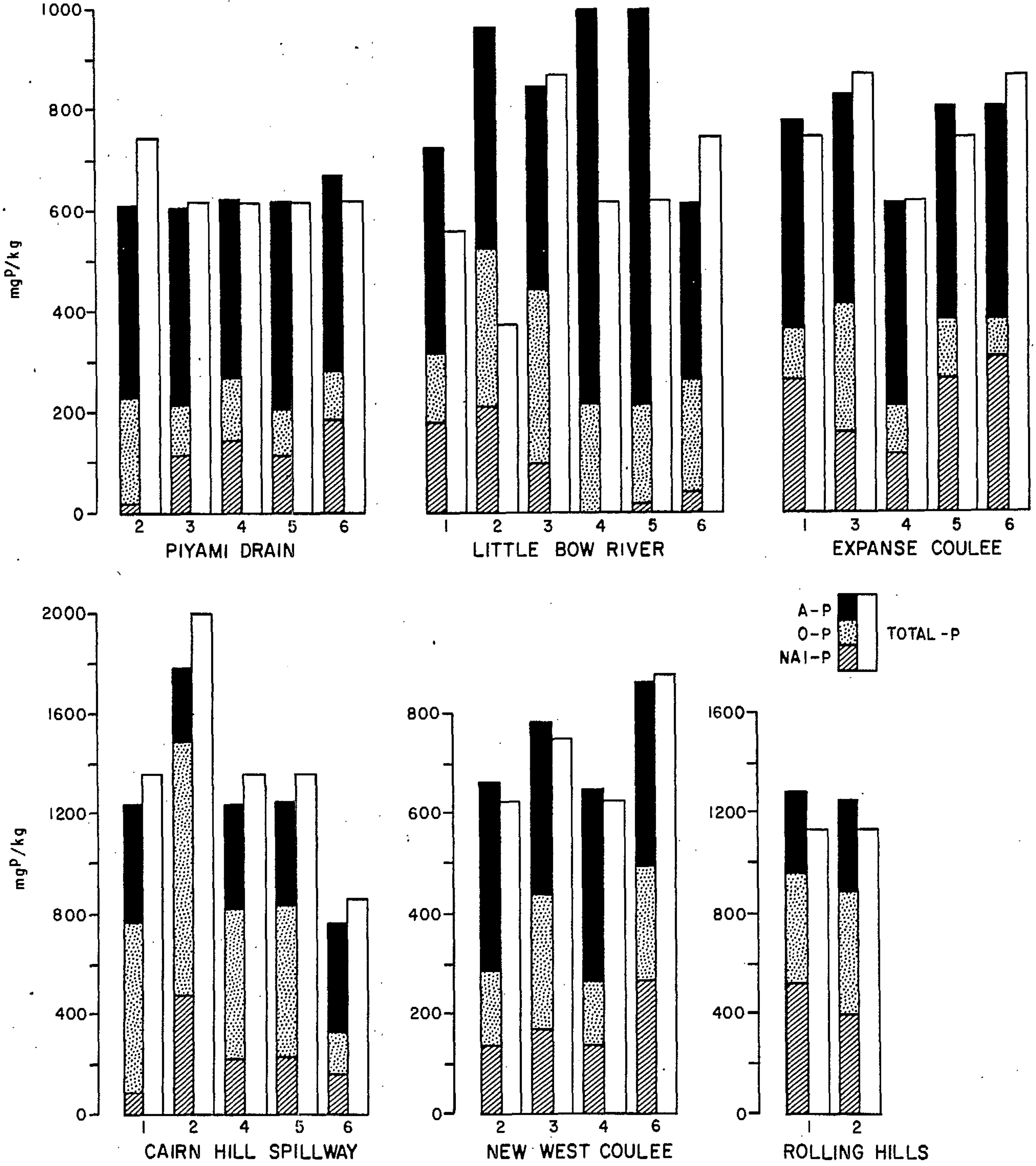

Figure 29. Phosphorus speciation on suspended sediment from selected irrigation return flows. The amount of each species (Williams *et al.*,1976) can be calculated using the ordinate axis scale. Difference between T-P and the sum of NAI-P, O-P and A-P is a measure of analytic imprecision.

Phosphorus

Total dissolved-P in sampled irrigation return flows to the Bow River varies closely about a mean value of 0.43 mg/L. In reference to Figure 11 only in the most downstream locations does TDP in return-flow water exceed that found in summer and fall samples of the Bow River. Whether this exceedance is significant could only be determined by more frequent sampling. Our data indicate that TDP between Highway 36 (BR36) and Ronalane (BRR) is uniformly low regardless of inputs.

A similar situation exists for the Oldman River. TDP values are relatively high (mean of .072 mg/L) from Piyami Drain. These inputs occur, however, at a point immediately downstream from Lethbridge where the river TDP levels are already high (>.10 mg/L). TDP inputs further downstream from Expanse Coulee and Little Bow River (both approximately .032 mg/L) do not appear to affect the uniformly low values in the Oldman River at Taber (ORT) and Bow Island (ORBI).

Suspended sediment-associated phosphorus (Figure 29) is much less than that found in Bow and Oldman River suspended sediments. River sediments display pronounced seasonality in P-enrichment (Figure 12) with lowest values in spring when rivers are loaded with sediment of diffuse-source origin having essentially background levels of phosphorus. Total-P on irrigation return flow sediments are similar in all seasons to spring data on both rivers, and have a substantial portion (often exceeding 50%) as apatite-P (A-P). The apatite fraction is especially large in those return flows with a substantial sand fraction (Figure 28) and in Piyami Drain with its extremely large suspended sediment concentrations. Despite low organic content in return-flow suspended sediments the organic-P (O-P) fraction is generally quite sizable. The NAI-P fraction is generally <200 mg/kg for those flows to the Oldman River and <300 mg/kg for those tributary to the Bow. These contrast with NAI-P concentrations of some 1000 mg/kg in summer and fall on Bow River sediments, and 500 mg/kg on Oldman River sediments. By comparison, river sediments in summer and fall have been enriched in NAI-P by a factor of x2 to x3.

As a general conclusion, suspended sediments in irrigation return flows throughout the 1980 sampling period are not enriched. They are similar in T-P and their relative proportions of A-P, O-P and NAI-P to suspended sediments in spring in both rivers. Irrigation return flows are not, therefore, responsible for observed loadings of phosphorus-enriched sediment found in summer and fall in either the Bow or Oldman Rivers.

Heavy Metals: Water

Nine heavy metals (Cu, Mn, Zn, Fe, Co, Ni, Pb, Cd, & Cr) were analyzed for Total and Filterable concentrations. Using a concentration factor of x10, only Cu, Mn and Fe were detectable in all filtered samples (Zn was excluded because of contamination of the filtered sample). With the same concentration factor Pb and Cd could not be detected in any of the Total samples, while Ni, Co and Cr were detectable in only a few of the Total samples. For the purpose of tabulation of metals, therefore, only Cu, Mn, Zn and Fe are included in Table 9.

Table 9 contains the mean and range for all detectable Total and Filterable metals in water samples. Most locations appear to have comparable levels of metal concentrations. Piyami Drain, with its large suspended sediment concentrations, has substantially higher levels of Total metals than at other sites. Iron levels are largest by almost an order of magnitude. The other detectable metals fall in order from Mn, Zn to Cu. The exception to this is Coal Creek where unfiltered Zn and Cu are comparable, with copper values frequently exceeding those of zinc. All metal levels in unfiltered waters from Rolling Hills, Coal Creek and Twelve Mile Coulee are substantially less than at other sites. The metals Ni, Co, Cr, Pb and Cd were less than detection in too many instances to discern any trends. Nickel, Co and Cr were detected only on the first sampling runs at Piyami Drain, Little Bow River, Expanse and New West Coulees. This is consistent with the elevated levels of other metals at that time. In general, metal concentrations at locations having considerable suspended solids tend to decrease from spring to fall.

As for river data, there appears to be a clear chemical distinction between those sites having high levels of suspended sediment concentration and those without. The average suspended sediment concentrations in Table 8 display large differences between the group of flows consisting of Coal Creek, Twelve Mile Coulee and Rolling Hills Canal (<15 mg/L) and all other locations (>100 mg/L). The latter group have much higher Total metal values reflecting the influence of suspended matter. Metal values are exceptionally high at Piyami Drain with its very large sediment concentrations (mean of 444 mg/L). In comparison, those sites with <15 mg/L (Rolling Hills, Twelve Mile and Coal Creek) have Total metal values which are up to an order of magnitude less than at the other sites.

Seasonal trends for Total metals for those sites with substantial suspended sediment tend to illustrate a general decline from spring to fall. The other sites show only a minor decline. Filtered data for Bow River return flows show no seasonal trends whereas those on the Oldman have a general rising trend into the fall of 1980.

Heavy Metals: Suspended Sediment

An estimate of sediment-associated metals can be obtained by the difference between Total and Filterable metals (Table 8). Iron is almost exclusively associated with sediment, as is Mn to a large degree and, to a much smaller extent, Cu. Sediment-associations are dependent upon suspended sediment concentrations as seen in Table 8.

All suspended sediment samples were analyzed for "total" metal content for Cu, Mn, Zn, Fe, Co, Ni, Cr, Pb and Cd using hot nitric acid - hydrochloric acid digestion. This is the same method as noted above for river sediments. In subsequent speciation studies (noted below) Cd was not analyzed as it was at or below detection in the "total" extraction.

Measurements of the nine heavy metal concentrations on suspended sediment were made over the irrigation season from those five irrigation return flows having sufficient suspended matter for collection purposes (Piyami Drain, Little Bow River, Expanse Coulee, New West Coulee and Cairn Hill Spillway). Because of very low sediment concentrations Rolling Hills distribution canal was sampled only twice (June 18 and July 3, 1980). The data from Rolling Hills are not dissimilar to return flow data.

Sediment-associated heavy metals are plotted in Figure 30. The lines joining the data points are for ease of interpretation and only

TABLE 9. Summary Table for Unfiltered (Total) and Filtered Metal Concentrations in Water Samples, ug/L (Range, Mean Values).

Site		Cu	Mn	Zn	Fe
BOW RIVER SYSTEM					
Cairn Hill Spillway	UF	3- 6, 5	21-118,68	9-29,14	380-2000,1447
	F	1- 5, 3	3- 9, 7	*	34- 81, 52
Coal Creek	UF	2- 9, 4	6- 52,18	2- 7, 4	102- 630, 212
	F	2- 4, 3	5- 13, 8	*	37- 75, 55
New West Coulee	UF	3- 9, 6	32-165,99	8-28,16	1000-6200,2900
	F	2- 4, 3	4- 9, 5	*	8- 23, 28
Twelve Mile Coulee	UF	1- 4, 2	16- 41,31	2- 8, 5	118- 420, 246
	F	2- 3, 3	9- 19,12	*	24- 53, 36
OLDMAN RIVER SYSTEM					
Piyami Drain	UF	4-22,12	37-440,202	7- 76,39	1200-14600,6500
	F	1- 6, 4	2- 9, 5	*	13- 95, 61
Little Bow River	UF	4-10, 6	39-164,82	8- 30,16	1200-6800,3200
	F	3- 9, 5	4- 8, 6	*	12- 112, 46
Expanse Coulee	UF	4- 7, 6	73-120,91	8- 25,14	1200-2500,1900
	F	2- 8, 5	6- 31,13	*	15- 27, 23
DISTRIBUTION CANAL					
Rolling Hills	UF	2- 3, 2	8- 21,13	2- 17, 6	105- 226, 159
	F	2- 4, 3	3- 2, 3	*	33- 16, 23

Note: Detection limits were

Cu	1 ug/L	Co	5 ug/L
Mn	1 ug/L	Ni	5 ug/L
Zn	1 ug/L	Cr	2.5 ug/L
Fe	1 ug/L	Pb	10 ug/L
		Cd	1 ug/L

: All values for Co, Ni, Cr, Pb and Cd were below these set detection limits for all samples

* Contaminated samples, values contained in Appendix IV Table 2.

TABLE 10. Summary Table for Suspended Sediment-Associated Metals (Range, Mean) ug/g.

		Cu	Mn	Zn	Fe
Piyami Drain	HNO_3-HCl	20-30,26	415-570,490	71-104,85	17700-25000,20730
	10% HCl	8-11,9	323-393,366	37- 49,44	740- 910, 790
	2.5% HCl	6- 8,7	312-367,340	23- 30,27	290- 390, 340
	$MgCl_2$	<1	2- 9, 5	<.5	1- 2, 1
Little Bow River	HNO_3-HCl	20-46,32	350-605,490	41-105,80	11000-25500,19100
	10% HCl	8-18,12	293-420,367	23- 49,38	470- 850, 680
	2.5% HCl	7-12, 9	289-385,332	17- 32,24	260- 390, 343
	$MgCl_2$	<1	4-26, 15	<.5	<1- 2, 1
Expanse Coulee	HNO_3-HCl	9-41, 25	315-1060,705	26-114,76	7800-26000,18100
	10% HCl	7-11, 9	369- 695,513	24- 56,37	500- 830, 650
	2.5% HCl	6-10, 7	290- 648,450	14- 42,25	220- 400, 300
	$MgCl_2$	<1	13- 84, 33	<.5	<1- 6, 2
New West Coulee	HNO_3-HCl	19-75,32	370-790,475	67- 87,79	14900-19400,17000
	10% HCl	8-11, 9	320-373,340	35- 41,37	670- 820, 735
	2.5% HCl	6- 9, 8	287-319,304	18- 22,20	310- 340, 330
	$MgCl_2$	<1	6- 80, 25	<.5	1- 4, 2
Cairn Hill Spillway	HNO_3	20-52,30	650-870,680	84-159,107	16900-29500,21100
	10% HCl	11-11,11	662-801,715	60- 69,64	890- 1000, 950
	2.5% HCl	8-10, 9	502-751,651	43- 53,47	470- 560, 510
	$MgCl_2$	<1	45-108, 71	<.5	3- 19, 6

		Co	Ni	Cr	Pb
Piyami Drain	HNO_3	8-12,10	22-30,26	19-26,23	10-13,12
	10% HCl	6- 7, 6	13-16,14	5- 8, 7	8-11, 9
	2.5% HCl	4- 6, 5	8-11, 9	2- 4, 3	6- 9, 8
	$MgCl_2$	<1	<1	<1	<2
Little Bow River	HNO_3	5-12,10	13-30,23	12-27,20	9-15,12
	10% HCl	5- 7, 6	9-14,13	3-10, 6	6-13,10
	2.5% HCl	2- 5, 4	7-10, 8	2- 3, 2	6-11, 8
	$MgCl_2$	<1	<1	<1	<2
Expanse Coulee	HNO_3	4-10,8	9-25,19	7-21,16	6-14,10
	10% HCl	4- 6,5	8-13,10	4- 6, 5	6-12, 8
	2.5% HCl	4- 4,4	4- 7, 6	<2- 2, 2	5-10, 7
	$MgCl_2$	<1	<1	<1	<2
New West Coulee	HNO_3	8-11,9	18-22,19	15-22,18	10-12,11
	10% HCl	6- 7,7	12-14,13	4- 5, 4	9-10,10
	2.5% HCl	5- 7,6	9-10,10	<2- 2, 2	7- 7, 7
	$MgCl_2$	<1	<1	<1	<2
Cairn Hill Spillway	HNO_3	8-10,9	20-28,25	18-33,23	13-20,15
	10% HCl	6- 7,7	15-17,16	7- 8, 7	14-16,15
	2.5% HCl	5- 6,6	11-12,11	3- 4, 3	11-12,11
	$MgCl_2$	<1	<1	<1	<2

DETECTION LIMITS

	Cu	Mn	Zn	Fe	Co	Ni	Cr	Pb	Cd
HNO_3	2	10	2	50	4	4	4	4	.5
10% HCl	.5	1	.5	10	1	1	1	2	
2.5% HCl	1	1	1	10	2	2	2	4	
$MgCl_2$	1	1	.5	1	1	1	1	2	

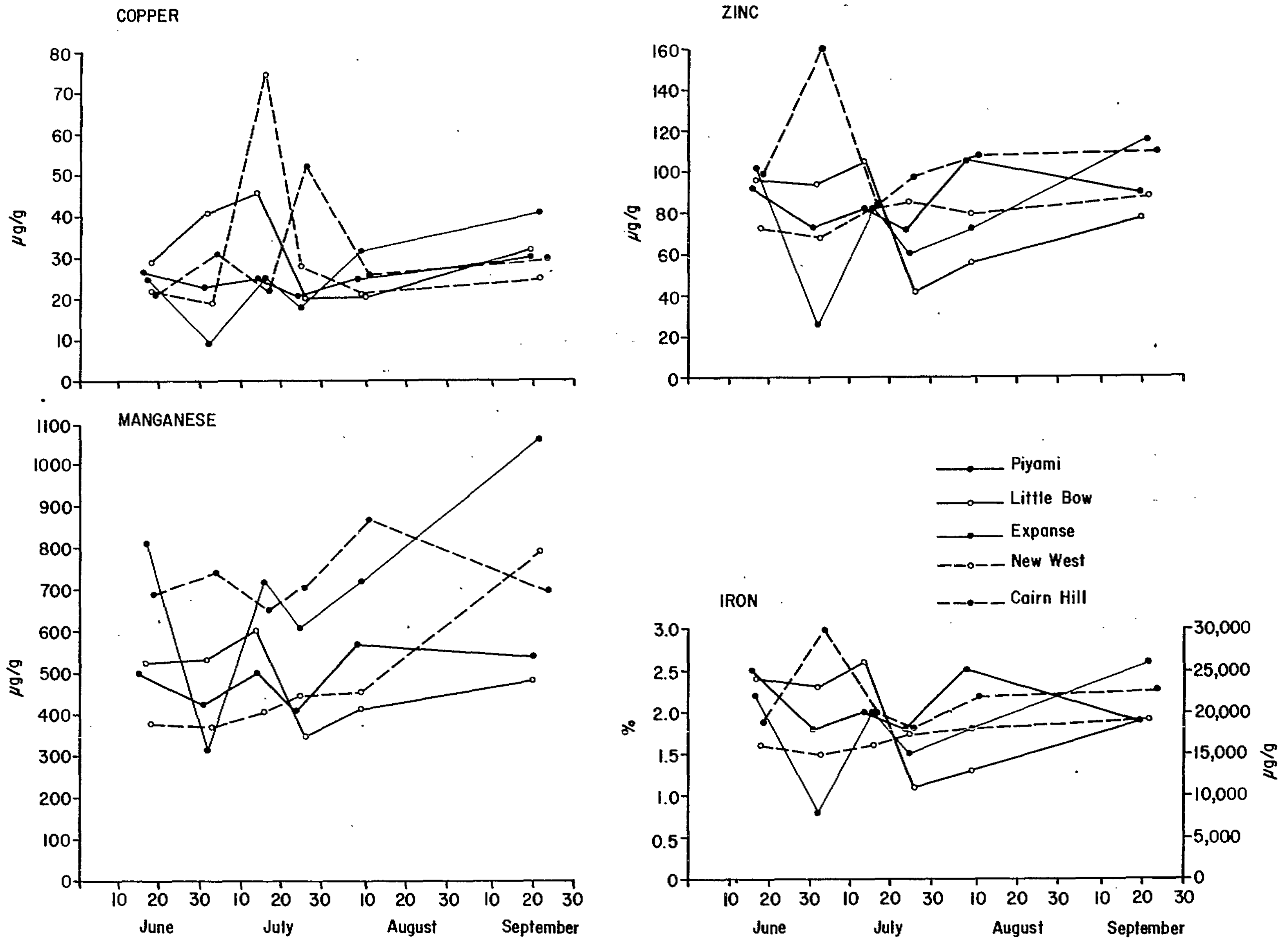

Figure 30. Suspended sediment-related metals concentrations in irrigation return flows.

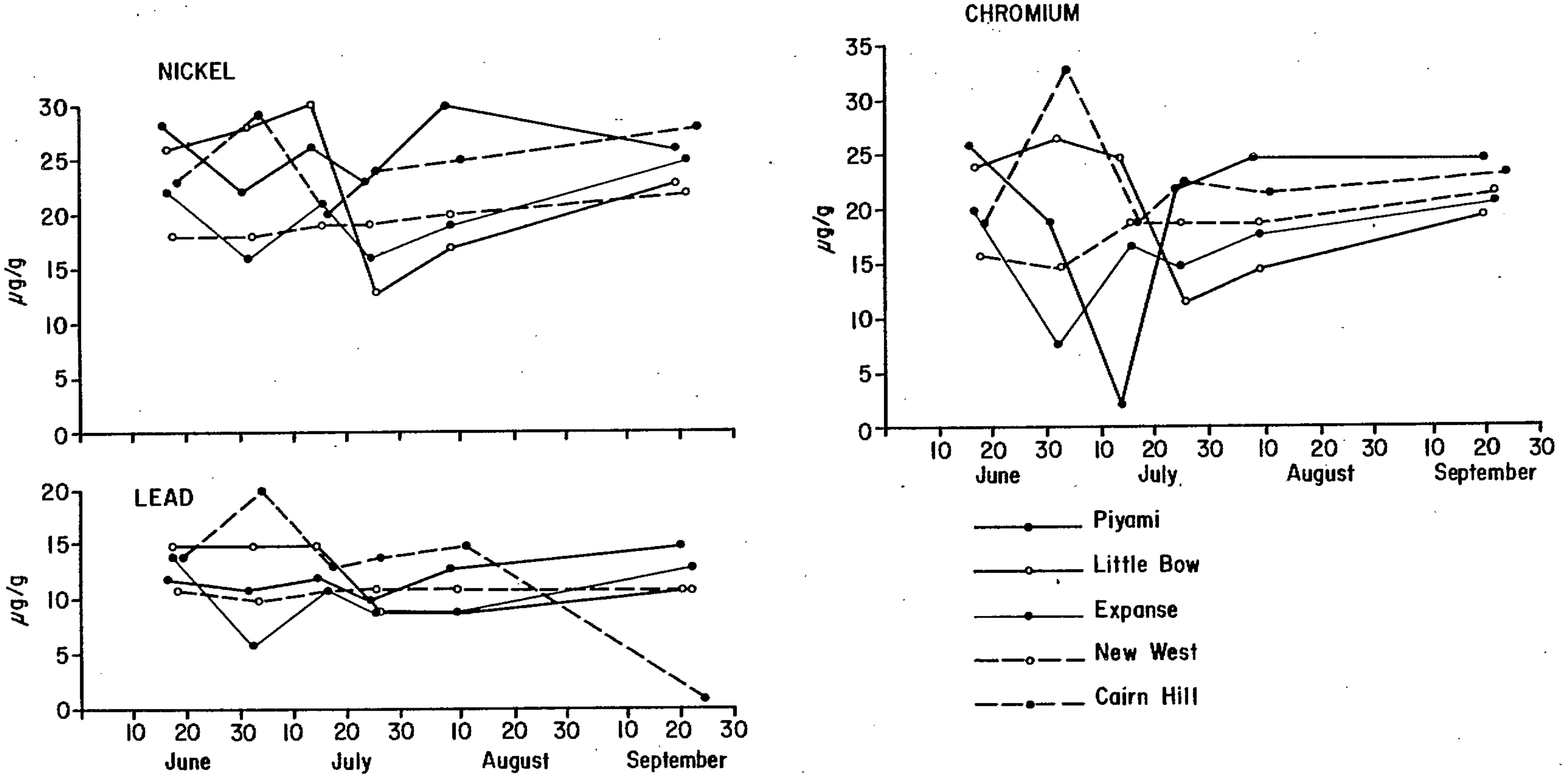

Figure 30. (Cont'd.)

suggest general trends. Summary numeric data for all digestion procedures are reported in Table 10. The main points to be drawn from Figure 30 and Table 10 are:

(1) There appears to be relatively little change in the concentration of any metal over the season. Maximum variance occurs early in the season and, with the exception of Mn, all metals at all sites converge towards the end of the season.

(2) At all sites, Fe was the most dominant element, followed by Mn. Metals decrease in concentration in all sites as:

$$Fe > Mn > Zn > Cu > Ni > Cr > Pb > Co$$

Cadmium was not detectable on sediment at any site.

(3) Metal concentrations exhibit substantial covariance. As is noted below, covariance tends to indicate that metal concentrations are produced by background chemistry rather than anthropogenic influences.

(4) Variance by element at each site is indicated by the standard deviations noted in Table 11. Using the coefficient of variation to indicate variance in one element relative to other elements (for all sites), only Cu shows a variation from the mean by more than 30%. Variability of all elements (with the exception of Cu) is <25%. Variability of Cu is 40%. Nickel, Cr and Pb are the least variable of the metals.

Heavy Metal Speciation: Suspended Sediment

Partial extractions of sediment-associated metals were used to examine the degree to which metals are likely to become available in the environment. The extractions are selective but not sequential; each extraction was carried out on a separate sub-sample. Increasingly rigorous extractions will reflect the cumulative amount of metal extracted by all less rigorous extractions. The amount of metal extracted by any one exractant can be estimated by subtracting amounts extracted by weaker extractants.

Quantity of freeze-dried material was a limited factor. Therefore partial extractions were carried out only on a selection of the sediment samples (Table 12).

The extractions performed were:

(1) hot concentrated HNO_3-HCl : This effectively oxidizes organic matter, dissolves precipitated and adsorbed metals and leaches certain metals from the detrital silicate structures. This digestion reflects the concentration of total metal present in a sample with the exception of metals tightly bound in the silicate lattice (Agemian and Chau, 1976).

(2) cold (room temperature) 10% HCl: This was examined as an alternative to hot HNO_3-HCl.

(3) cold 2.5% HCl: This extracts metals bound into carbonate structures and which can become available in certain aquatic environments (Forstner and Wittmann, 1981).

(4) 0.5M $MgCl_2$: This estimates the readily exchangeable fraction (Gibbs, 1977; Tessier et al.,1979).

The distribution of metal species is noted in Figure 31. These are averages of the sample data noted in Table 10. Using copper as an example, the interpretation of Figure 31 is: $MgCl_2$ extracts <4% of the total (hot HNO_3-HCl extractable) metal; 2.5% HCl extracts the <4% ($MgCl_2$) plus an additional 32% of the total; 10% HCl extracts the <4% + 32% plus an additional 09%; the remaining 57% is only extractable with hot HNO_3-HCl.

In general, the labile fraction ($MgCl_2$) is exceedingly small. In many instances this component was not detectable; in this circumstance the concentration was arbitrarily set at half the detection limit. The largest fraction is the residual fraction (only extracted by hot HNO_3-HCl) with the second largest fraction generally associated with carbonates (2.5% HCl). Notable exceptions are Pb, Mn, Ni, Co for which the largest fractions appear to be carbonate-associated.

As a general conclusion, metals appear to bound up as part of an organo-mineral complex. The exchangeable fraction is very low. Similarity of CaO content (Appendix 1) of river sediments with those of southeastern Ontario (Ongley et al.,1981) suggest that the carbonate-associated metals may be bound into secondary amorphous and cryptocrystalline deposits. This assumption would require further verification. The degree to which these metals could become available

TABLE 11. Standard Deviations* (s), Mean Values (x) and Coefficients of Variation** (V) for Suspended Sediment-Associated Metals.

Site		Cu	Mn	Zn	Fe	Cd	Ni	Cr	Pb	N
Piyami Drain	s	3.6	61.5	12.3	3377.4	1.6	3.2	2.8	1.2	6
	x	26	490	85	20730	10	26	23	12	
Little Bow River	s	10.7	91.7	39.1	6061.5	2.4	6.5	5.9	3.0	6
	x	32	490	80	19100	10	26	23	12	
Expanse Coulee	s	11.1	244.9	31.4	6191.2	1.6	3.2	2.8	1.2	6
	x	25	705	76	18100	8	19	16	10	
New West Coulee	s	21.5	229.3	7.5	1519.2	2.5	1.5	2.5	0.6	6
	x	32	475	79	17000	9	19	18	11	
Cairn Hill Spillway	s	11.5	75.6	27.6	4758.6	0.9	3.4	5.4	2.7	6
	x	30	680	107	21100	9	25	23	15	
	V	40%	25%	28%	23%	20%	16%	19%	14%	

* Standard Deviations $s = \sqrt{\frac{(\bar{x} - x)}{(n - 1)}}$

** Estimate of coefficient of variation $V = \frac{\text{Mean of standard deviations}}{\text{Mean of site means}}$

N = number of samples

TABLE 12. Selected Suspended Sediment Samples for Partial Extractions.

Site	Date	Extractions Performed*	Organic Carbon Content (%)
Oldman River System			
Piyami Drain	16/06/80	MC, WA, SA	1.5
	01/07/80	MC, WA, SA	1.3
	14/07/80	MC, WA, SA	1.6
	23/07/80	MC, WA, SA	1.6
	08/08/80	MC, WA, SA	1.1
	20/09/80	MC	
Little Bow River	17/06/80	MC, WA, SA	1.6
	02/07/80	MC	
	14/07/80	MC	
	24/07/80	MC, WA, SA	1.1
	09/08/80	MC, WA, SA	1.6
	20/09/80	MC, WA, SA	2.0
Expanse Coulee	17/06/80	MC, WA, SA	3.1
	02/07/80	MC, WA, SA	0.7
	16/07/80	MC	1.2
	25/07/80	MC, WA, SA	1.0
	09/08/80	MC	1.7
	22/09/80	MC	
Bow River System			
New West Coulee	18/06/80	MC, WA, SA	1.2
	03/07/80	MC, WA, SA	1.3
	16/07/80	MC, WA, SA	1.5
	25/07/80	MC	
	09/08/80	MC, WA, SA	1.9
	22/09/80	MC	2.6
Cairn Hill Spillway	19/06/80	MC, WA, SA	4.2
	04/07/80	MC	6.6
	17/07/80	MC, WA, SA	4.6
	26/07/80	MC	
	11/08/80	MC, WA, SA	6.4
	24/09/80	MC	5.6
Distribution Canal			
Rolling Hills	16/06/80	MC	
	03/07/80	MC	

*Note: MC is 0.5N $MgCl_2$ extraction
WA is 2.5% HCl extraction (weak acid)
SA is 10.% HCl extraction (strong acid)

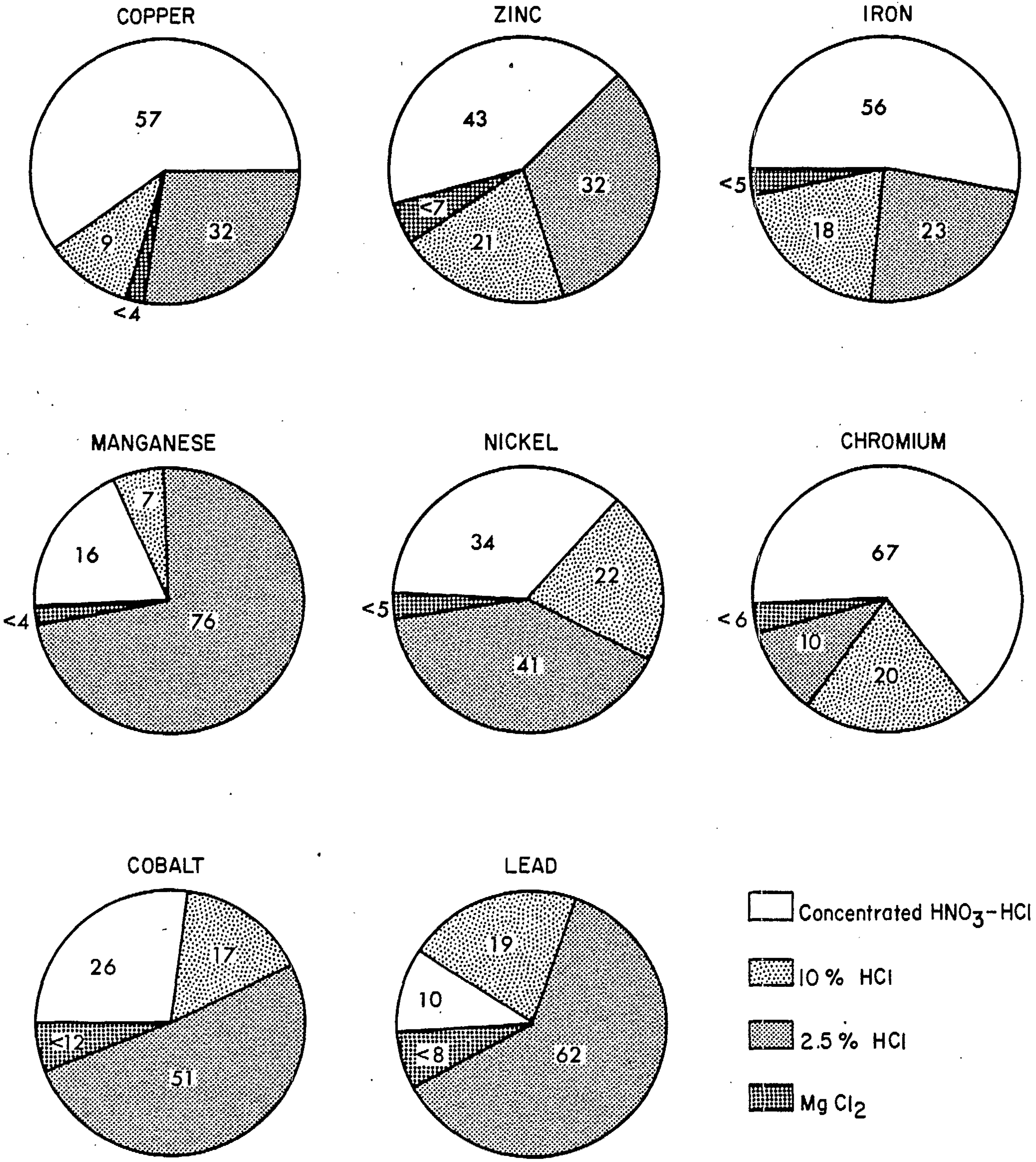

Figure 31. Increment of metal extracted by increasingly rigorous extractions. Values are relative to Total metal extracted by hot HNO_3. Data are averages for all sites in Table 12.

would depend upon pH and temperature conditions in a sink environment.

Data published for prairie soils (Dudas & Pawluk, 1977: Mills & Zwarich,1975) suggest that sediment-associated metals in irrigation return flows are similar to metal concentrations found in typical prairie soils. We conclude, therefore, that suspended sediments from irrigation return flows are not enriched and represent essentially background levels of metal chemistry. This inference is supported by the high degree of similarity (low variance and coefficients of variation) of sediment-associated metals from irrigation return flows representative of a broad range of natural and anthropogenic conditions. Furthermore, the order in which trace metals occur at all sampled sites is nearly identical (Fe > Mn > Zn > Cu > Ni > Cr > Pb > Co). The last few elements are subject to some interchange between sites but the trend is consistent overall.

SUMMARY AND MANAGEMENT IMPLICATIONS

The objectives of the study were, in part, to assess seasonally-variant biogeochemical pathways in fluvial systems in the context of efficiency of conventional monitoring information to identify patterns and causality of nutrient and contaminant stress in the aquatic ecosystem. The principal management issues in these two rivers are:

1. Major point sources on each river (Calgary on the Bow and Lethbridge on the Oldman River).

2. Excessive marcrophyte growth in nutrient-rich waters of the Bow and which extended in 1979 as far downstream as the confluence of the Bow with the Oldman River.

3. Diversion of large volumes of river water for irrigation with accompanying deoxygenation and periodic fish kills in reaches with very low dicharge downstream from abstraction points.

4. Return to the Bow and Oldman Rivers of surplus irrigation water and the potential for anthropogenic inputs from irrigated agricultural surfaces.

5. The extent of downstream impact of Calgary on water quality in the Bow and the perception of riparian users downstream from Bassano that degraded water is a direct result of Calgary effluents. This applies both to water diverted to Lake Newell (Brooks water supply) and that which flows further downstream in the Bow River.

6. Conflict between the view that a river provides cost-free tertiary treatment versus the demand for a recreational resource of good-quality water.

7. Loadings of nutrient and contaminants delivered to the South Saskatchewan River and which comprise an external loading to

reservoirs further downstream.

8. A more general question of the ability of conventional water quality surveillance data to address these issues.

Other management concerns not addressed in this study but which may have significant impact on these two rivers are:

a. expansion of irrigated areas and demand for larger diversions from these two rivers.

b. use of underdrainage (tile drains) to reclaim salinized soils no longer in production.

c. major interbasin diversions.

d. increasing industrial use of river water which will accompany western industrial expansion.

e. impact of long-term drought on aquatic health in the face of competing demands for water.

This study does not deal equally with all eight points noted above. It does not touch upon #3 and deals only marginally with the general question of relationship between nutrient abatement and biomass productivity which is the subject of extensive research by Alberta Environment.

We do not make extravagant claims concerning representivity of our data. With only one sampling run per hydrologic season we claim only that our data are characteristic of the type of conditions which exist in each season. Because river regimes and, especially, the suspended sediment component change dramatically over the year, quantum changes are captured by the type of data collected here.

Suspended Sediment

Over the six month period (May-Oct) for which we have data, water chemistry is significantly influenced by suspended sediment. For most elements the six-month load is largely delivered during the two months of high water. During this brief period, the influence of Calgary and Lethbridge cannot be detected in the downstream direction because of large tributary inputs of suspended sediment. High `total´ element concentrations are produced almost without exception by the large amounts of sediment included in this analysis. Filterable concentrations of many heavy metals are not detectable either in spring or at other times. The correspondence of suspended sediment chemistry with bank material indicates that suspended sediment chemistry is generally at background levels during spring high flow and is not of biological relevance in these rivers. Further evidence from suspended sediment in irrigation return flows indicates that sediment inputs are representative of prairie soils and are not significantly enriched.

During low flow periods when suspended sediment concentrations are very low, urban inputs from Calgary and Lethbridge can be easily detected immediately downstream. There is, however, indirect but consistent evidence which suggests that subsequent downstream decreases in `total´ and `filterable´ levels of phosphorus and detectable heavy metals are due, at least in part, to dilution of enriched suspended matter by bank collapse and tributary inputs of unenriched sediments. Interpretations involving biouptake etc. to explain downstream reductions of nutrient and contaminants must , therefore, be treated with caution unless, as in this study, direct measurements of contaminants and of organic phosphorus and NAI-P are made on sediments and biomass.

Phosphorus: Water

Total Phosphorus is dominated by particulate-associated phosphorus during high water periods. At other times TP and TDP initially increase below Calgary and Lethbridge and then decline downstream. As these decline there is a progressive loss of TDP with commensurate increase in the proportion of TP associated with particulate matter. This suggests conversion of dissolved phosphorus to particulate form by physico-chemical processes. In summer and fall, TDP is reduced to BR85 (background) levels by BR36, a river distance of some 240 km.. Total phosphorus values, however, are significantly higher than background. The extent of downstream reduction in TP and TDP in the Oldman River is different in summer and fall and cannot be generalized from our data.

Total and filterable phosphorus are useful measures in characterizing spatial and temporal changes in phosphorus flux. For management purposes both variables are required in order to characterize:

(a) the conversion of TDP (as a surrogate for bio-available P) to particulate form,

(b) the loss of phosphorus load as TP concentrations change in a downstream direction,

(c) the total phosphorus flux, given that the particulate fraction does contain phosphorus which can become bio-available under certain sink conditions.

Limitations: Loss of phosphorus in the downstream direction is in part explained by bioaccumulation in plant tissue. As noted elsewhere, total phosphorus loadings stored in plant tissue in the Bow River may exceed measured chemical load by several orders of magnitude.

Phosphorus: Suspended Sediment

The particulate load is comprised of unavailable apatite-P, and potentially available NAI-P and O-P. While these latter two forms are not important in a riverine environment, they can be significant in a sedimentary environment, especially under reducing conditions. Large apatite loads dominate the particulate-P load during spring high water periods. At other times of the year the distribution of sediment-associated phosphorus species is very different from that found in spring.

For downstream management purposes, sediment-associated phosphorus forms should be characterized on a seasonal basis at the most downstream point within an agency's jurisdiction. Our data and other related experience indicated that there is little variability between sites during high flows in spring so the choice of site at that time is probably not critical. At other times of the year there is progressive downstream change; therefore, choice of site becomes important. For management purposes, it is only necessary to characterize phosphorus species on a few sediment samples. While temporal and analytical variation can be expected from any one site over a single hydrologic season, it is not cost-efficient nor scientifically defensible to determine speciation variance in view of the many other forms of variance which are introduced in the process of calculating a sediment-associated phosphorus load over an extended period. It should be recalled that the calculation of sediment loads are notoriously inaccurate (Ongley et al. 1977).

For most management purposes adequate spatial characterization of phosphorus can be obtained by TP and TDP. Although TDP is not directly related to SRP (bioavailable P), TP-TDP does measure the change from solute to unavailable (in rivers) phosphorus. This is important, especially as our data indicate that there is a large and potentially (in a reservoir context) available sediment-associated phosphorus load in low-flow months when suspended sediment concentrations are very low (e.g., 56 tonnes at Ronalane in the Bow River).

Phosphorus: Aquatic Plants

For management purposes aquatic plants are a mixed blessing. On the one hand they extract phosphorus (and other elements) from the water column, thereby effecting in-stream tertiary treatment. On the other hand, they accumulate astonishing loads of phosphorus which can be released back to the aquatic system during senescence. As there is no permanent sink for organic detritus in a flowing system, the decay products are transported downstream to the next reservoir in which there is a sedimentary environment. The degree to which this form of transport is a significant factor in reservoir enrichment is not known, partly because it has not, to our knowledge, been studied and partly because it would depend upon the sedimentation rate and limnologic conditions of the receiving water body.

For monitoring purposes, phosphorus concentration in macrophytes appears not to be a useful indicator of nutrient stress. Firstly, total-P in plants reflects not only bioassimilated-P but also phosphorus associated with entrapped suspended matter as well as other phosphorus forms associated with precipitates etc.. Secondly, although there are some changes in the organic phosphorus fraction, the amount of O-P in plants is quite constant (1400 to 1600 mg/kg) due to luxury uptake regardless of site conditions. Nutrient stress appears to be reflected in plant density and plant size. Because bottom sediments are too coarse to provide any significant nutrient source to aquatic plants in either river, productivity in nutrient-poor environments appears to be controlled by seeding from upstream. Because of luxury uptake, plants can survive for extended periods in nutrient-poor water. Sewage control programs should not, therefore, ignore the impact of short-term releases of nutrient-rich effluent which may make other control programs counter-productive.

Efforts to model productivity using chemical data should take into account, therefore, the influence of downstream seeding by opportunistic species and the frequency, duration and seasonality of uncontrolled effluent discharges. Also, it should be noted that the hydraulic behaviour of the Bow River during high flow serves to disrupt and/or destroy the rooting environment of macrophytes. In this sense, river hydrology serves as a natural control on macrophyte growth over the longer term.

The determination of phosphorus loadings in rivers having a significant macrophyte or algal population requires the measurement of biomass and plant-associated phosphorus. As noted above, the accumulation of phosphorus load in the Bow River below Calgary is up to two orders of magnitude higher than that measured as chemical flux by conventional variables.

Phosphorus: Irrigation Return Flows

Total dissolved phosphorus in irrigation return flows is not elevated relative to receiving waters except in some downstream locations. Nevertheless, our data suggest that there is no change in downstream levels of TDP in river waters at downstream sites. We conclude that the sampled irrigation return flows are marginal contributors of dissolved-P to the Bow and Oldman Rivers and are probably not significant in terms of other contemporary sources of phosphorus. Whether they would become significant should there be a dramatic decline in urban point sources would require further study.

Sediment-associated phosphorus species in irrigation return flows are very similar to that found on suspended sediments in rivers in spring. We conclude that, over the irrigation season, suspended sediments are not enriched and do not materially add to the nutrient load of either the Bow or Oldman River.

Heavy Metals: Water

Most filterable and many `total' metals exist at concentrations below conventional detection limits. In spring, metal levels tend to be approximately ten-fold higher than in other seasons, mainly due to the high concentrations of suspended matter and, to a lesser extent, due to changes in particle-size distribution. As noted elsewhere, suspended sediment chemistry reflects unenriched sediments of diffuse source origin from eroding prairie and foothill surfaces.

Detectable total metals in spring tend to illustrate an increasing downstream concentration reflecting sediment inputs from tributaries. At other times of the year the water data for trace metals are too incomplete to determine metal behaviour in space or time. This a serious and limiting attribute of conventional chemical measures. For other metals such as Zn and Cu which are found in detectable concentrations, water chemistry provides no clearly-defined downstream trends nor, with the exception of spring data, pronounced seasonal differences. By comparison, suspended sediment and plant data both illustrate spatial trends and, for suspended matter, clear seasonal differences.

Heavy Metals: Suspended Sediment

As a general observation, metals on solids show significant enrichment immediately below the two urban areas during low flow periods. By comparison, spring data show lowest metal concentrations reflecting sediment inputs of diffuse source origin from tributaries.

The chemistry of spring sediments is very much like sampled bedrock into which the rivers are incised.

The behaviour of sediment-associated metals during low flow below Calgary and Lethbridge varies amongst metals. In general, there is a peak below these centres followed by a decline. Iron and manganese behave rather differently from the trace metals. Most metals illustrate a small peak at Bassano Dam suggesting that a variety of metals are mobilized from Bassano sediments during summer and fall. Significantly, peaks in sediment-associated metals at Bassano are paralleled by peaks in plant metal levels, suggesting that metal-mobilization occurs in plant accessible form. There is a similar peaking of several metals on suspended sediment and in aquatic plants at Taber on the Oldman River. Because there is no sedimentary source such as that at Bassano, we presume there is a significant point or diffuse source somewhere between Coaldale and Taber.

Because suspended sediment is mobile, the decline during low flow of sediment-metal concentrations downstream from point sources is surprising. It is unlikely that significant desorption occurs between BR2 and BRCY by which time many sediment-metals have returned to values close to those immediately upstream from Calgary (BR85). Reductions are likely caused by small additions of suspended sediment from tributaries in this reach. Similarly, reduction in sediment-metal concentrations below the secondary peak at Bassano may be explained by sediment inputs from bank collapse which occurs with considerable frequency in this lower reach of the Bow River. A similar explanation may apply to the reductions in sediment-metal levels below Lethbridge on the Oldman River where collapse of poorly consolidated bedrock banks is frequently observed.

Heavy Metals: Aquatic Plants

Unlike suspended sediment, macrophytes and filamentous algae are immobile and serve as natural integrators of ambient bioavailable chemicals in transit in the water column. Generally plants display similar downstream trends as sediment-associated metals, especially for Ni, Zn, Cd and Pb in macrophytes of the Bow River. Generally, elevated levels of metals in plants occur over short distances below a point source; they are not attenuated in the downstream direction as is the case for suspended sediment (because of mobility of suspended matter). Also, the amplitude of change in concentration from background to enriched is less than for suspended sediment-associated metals. Plant-associated metals in the Oldman River show peaks below Lethbridge and again (as noted elsewhere) at the Taber site.

Rooted macrophytes and filamentous algae appear to offer a useful alternative to conventional chemical measurements for the determination of patterns of heavy metal stress in these river systems. In part, this results from the integrating nature of metal uptake through time. Also, the concentration of metals in plants serves as a direct measure of bioavailable metal. A major disadvantage of conventional total metal analysis in water samples is that it does not indicate the fraction which is bioavailable; this is especially limiting when filterable metals are below detection. As our data show, metals which are not detectable are easily found in aquatic plants. Plant data indicate that bioavailable metals are diminished to nearly background levels by Carseland on the Bow River -- an observation which is not possible with water or suspended sediment chemistry.

Significant plant uptake, however, implies a major loading which is temporarily locked up in biomass. Indeed, with the exception of iron, loadings of metals in biomass exceed measured chemical flux by many times. While this is of little consequence for studied reaches, the potential for loading downstream sedimentary environments with degradable organic debris and consequent release of metals may be significant. As for phosphorus, the degree to which this may be a problem in the South Saskatchewan system is not known. It does imply however that metal (and phosphorus) loads calculated from conventional data are greatly in error regardless of the frequency of chemical measurement.

Heavy Metals: Irrigation Return Flows

Suspended sediment-associated metals in irrigation return flows exhibit a high degree of covariance and similarity of temporal trends. Speciation chemistry indicates that these metals are not labile although several metals are associated with the carbonate fraction. Sediments in return flows are not enriched and are similar to the metal chemistry of prairie soils as reported by others. We conclude that irrigation return flows are not a significant contributor of metals to the South Saskatchewan River system.

Organochlorine Residues

Our work, in part, was to establish the nature of pathways and distribution of a suite of nonionic pesticides, PCB, and chlorobenzenes within water, suspended sediment and aquatic plants in the Bow and Oldman Rivers. Pesticides, and PCB residues characteristically have low solubility, high adsorbtivity and are persistent. The chlorobenzenes are relatively soluble and volatilize more readily. Adsorption of organochlorine residues onto solids is a common mechanism by which they are removed from the aquatic medium and transported in the fluvial environment.

Water, suspended sediment and plant material were scanned for chlorobenzenes (including hexachlorobenzene), all common nonionic organochlorine pesticide residues including α, β and γ-HCH, α, γ and oxy-chlordane, aldrin, endrin, dieldrin, heptachlor, HE, methoxychlor, DDT and its metabolites, plus mirex, photomirex and PCB.

The following compounds were detected: 1,3,5; 1,2,4; 1,2,3 chlorobenzene, α and β HCH, α-chlordane, dieldrin; DDE/DDD/DDT, and PCB. Generally these were found at or near detection limits. Significantly, only the chlorobenzenes and α-HCH were routinely detectable in `total' water samples. The remaining detectable substances are associated primarily with suspended matter and/or plant material. Our results indicate that many organochlorine residues preferentially associate with one or more of the sediment/plant/water phases. These results may be interpreted as field-derived distribution adsorption constants (Kd) which express the partitioning of a compound between solid and water phases.

The management implications of the organochlorine residue levels lies largely in the practical application of suspended sediment and/or biomass as appropriate media for monitoring many residues which cannot be detected in bulk water samples. Although not investigated here, the potential use of aquatic plants for detection of modern, more soluble and degradable biocides is an avenue of great potential significance.

As noted for metals and phosphorus, large volumes of water and high suspended sediment concentrations of diffuse source origin in spring reduce (especially for chlorobenzene isomers) the ability to detect residues. This poses a dilemma for agencies insofar as the close association of residues of low solubility with suspended sediment implies that the bulk of the annual load of these substances occurs during short periods of high flow when these substances are most difficult to detect. Although plant-associated loadings of organochlorine residues were not calculated, it is likely that the consistent relationship of certain residues with plant matter represents a significant and unmeasured load of potential downstream consequence.

ACKNOWLEDGEMENTS

This study was funded by a combination of research grants and contracts from, variously, the Natural Sciences and Engineering Research Council of Canada (NSERC), research subventions from Inland Waters Directorate of Environment Canada, and research contracts from the Toxic Contaminants Management Program of Environment Canada. Many individuals and agencies contributed to this reseach program. In particular, Dr. R.J. Allan (at the time he was Chief, National Water Research Institute-Western and Northern Region) was largely responsible for arranging key financial support and for encouraging us to work in the very large river systems of Southern Alberta. Discharge data were provided by the Water Survey of Canada. Alberta Environment (Water Quality Control Branch) played a key role insofar as that agency was undertaking a parallel program on nutrient cycling and encouraged us to participate in the overall structure of their South Saskatchewan River program. Alberta Environment provided us with a boat and motor for the duration of our program, undertook analysis of TP and TDP in water samples and provided laboratory space at their Lethbridge facility. K. Exner and D.N. Graveland of Alberta Environment were especially accommodating in providing material support and advice. Mercury analyses on sediments and in water were kindly provided by Dr. A. Lutz and Mr. R. Woychuck, respectively. The material included in this final report is drawn mainly from MSc thesis research programs of H.C. Joseph and D.P.Blachford, graduate students in the Department of Geography at Queen´s University. Additional information on centrifuge operation is drawn from other research programs of the senior author (Ongley) and variously funded by Inland Waters Directorate, National Water Research Institute-Pacific and Yukon Branch, NSERC, and Saskatchewan Department of Environment.

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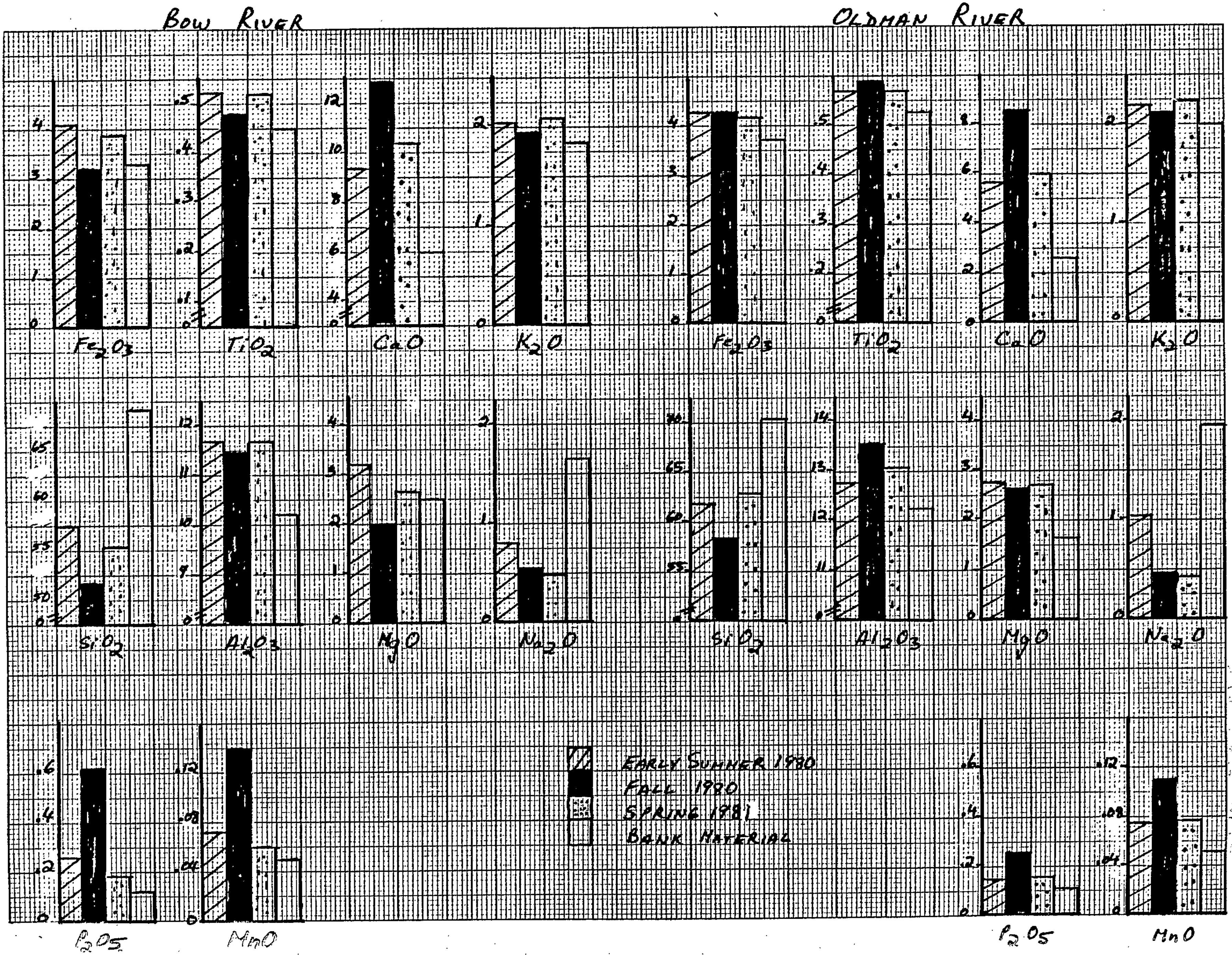
APPENDIX #1

ELEMENTS AS OXIDES BY X-RAY FLUORESCENCE

(Selected Samples)


BOW RIVER
OLDMAN RIVER
Fe_2O_3
0 1 2 3 4
TiO_2
0 .1 .2 .3 .4 .5
CaO
0 4 6 8 10 12
K_2O
0 1 2
SiO_2
0 50 55 60 65 70
Al_2O_3
0 9 10 11 12 13 14
MgO
0 1 2 3 4
Na_2O
0 1 2
P_2O_5
0 .2 .4 .6
MnO
0 .04 .08 .12
▨ EARLY SUMMER 1980
■ FALL 1980
▦ SPRING 1981
☐ BANK MATERIAL