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**Biogeochemical Pathways of  
Phosphorus, Heavy Metals and  
Organochlorine Residues in the  
Bow and Oldman Rivers,  
Alberta, 1980-1981**

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WATER QUALITY BRANCH  
OTTAWA, CANADA, 1984**

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**D.P. Blachford and E.D. Ongley\***

\*Chief, National Water Research Institute, Western and Northern  
Region, Freshwater Institute, Winnipeg.

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## Abstract

Spatial and temporal pathways of phosphorus, metals and organochlorine compounds in water, suspended sediments and plants were identified in the Bow and Oldman rivers. Sampling was carried out during the spring, early summer, summer and fall discharge regimes of 1980 and 1981. Seasonality of particle size and organic content was assessed. Pathways information was evaluated in terms of the ability of conventional water quality information to identify patterns and causality of nutrient and contaminant stress in the aquatic ecosystem.

Total and dissolved phosphorus measures characterize seasonal and downstream changes in phosphorus flux. Sediment-phosphorus speciation is required to identify phosphorus forms which are potentially available at downstream locations and at different stages of the hydrologic regime. Aquatic plants accumulate large quantities of phosphorus and represent a load significantly greater than that determined from conventional variables.

Total and filterable concentrations of metals are not useful in identifying spatial and temporal trends. Most filterable levels are below detection limits; total levels that are detectable reflect suspended sediment concentrations and particle size. Sediments and plants do indicate downstream changes in river chemistry. Plants are useful indicators of the available component of metal flux. Metal accumulation in plants implies a major loading which is temporarily held in biomass and which may be of downstream significance after decay of the organic material and consequent release of metals.

Organochlorine compounds associate with one or more of the water, sediment or plant phases. Conventional characterization of the compounds only in the water medium may greatly underestimate their presence.

## Résumé

Le cheminement spatio-temporel du phosphore, des métaux et des organochlorés dans l'eau, les sédiments en suspension et les plantes a été déterminé dans les rivières Bow et Oldman. Des échantillons ont été prélevés au printemps, au début de l'été, à l'été et à l'automne de 1980 et 1981. Le caractère saisonnier de la granulométrie et de la teneur en matières organiques a été établi. On a évalué les données sur le cheminement en fonction de la possibilité de déterminer, d'après les renseignements classiques sur la qualité de l'eau, les formes et les causes des perturbations causées par les éléments nutritifs et les contaminants dans l'écosystème aquatique.

Les mesures du phosphore total et dissous caractérisent les changements saisonniers et les changements en aval du flux du phosphore. Il faut déterminer les formes du phosphore dans les sédiments afin de connaître celles qui sont potentiellement disponibles en aval et à différentes phases du cycle hydrologique. Les plantes aquatiques accumulent de grandes quantités de phosphore qui constituent un stock passablement plus important que celui qu'on détermine par les variables habituelles.

Les concentrations des métaux totaux et filtrables ne sont pas utiles dans la détermination des tendances spatio-temporelles. La plupart du temps, les concentrations filtrables sont inférieures aux limites de détection; les quantités totales décelables reflètent les concentrations dans les sédiments en suspension et la granulométrie. Les sédiments et les plantes sont des indicateurs des changements de la chimie du cours d'eau en aval. Les plantes constituent des indicateurs utiles de la partie assimilable du flux de métaux. L'accumulation de métaux dans les plantes se traduit par un stockage important mais temporaire dans la biomasse, qui peut influencer notablement sur l'aval après la décomposition de la matière organique et la libération de métaux qui s'ensuit.

Les organochlorés peuvent se retrouver dans l'eau, les sédiments ou les plantes. Leur présence est considérablement sous-estimée par la méthode classique de caractérisation des composés uniquement à partir d'échantillons d'eau.

# **Biogeochemical Pathways of Phosphorus, Heavy Metals and Organochlorine Residues in the Bow and Oldman Rivers, Alberta, 1980-1981**

**D.P. Blachford and E.D. Ongley**

## **INTRODUCTION**

Effective protection of the aquatic environment demands an understanding of the processes governing the behaviour of nutrients and contaminants. Conventional water quality monitoring programs depend upon total and, where possible, filterable contaminant concentrations in water. Present monitoring practices characterize the ambient state of the water body at the time of sampling and are useful for monitoring of compliance of conservative substances for water quality objectives (Ongley, 1982a). The information produced, however, is inadequate not only for flow-dependent substances but also for comprehensive management of the aquatic system; it is also limited in its ability to describe spatial and temporal components of chemical flux in terms of both upstream source and downstream consequence. The focus on water chemistry generally precludes consideration of ecological factors and environmental impact.

There is a growing body of research on the use of sediments and aquatic biota to characterize water quality. In contrast with concentrations of contaminants in water, levels on sediments and in biota are considerably higher and are not only more easily detected but also permit chemical characterization of bioavailability and inferences concerning source. Association of contaminants with water, sediments and biota is controlled by seasonally and spatially variant physical and chemical characteristics of the fluvial environment. The chemistry of water, sediment and biota, therefore, more fully characterizes the quality of the aquatic system.

This study focusses on the Bow and Oldman rivers, two major tributaries of the South Saskatchewan River. Each river has one major point source: Calgary on the Bow, and Lethbridge on the Oldman River. 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 Calgary sewage outfalls and which in 1979 extended downstream to the confluence of the Bow and Oldman rivers. The reason for studying these

rivers was not dictated solely by local environmental issues but also by the lack of understanding of biogeochemical pathways of nutrients and contaminants in large rivers in general and in prairie rivers in particular. The study builds upon work completed in small and medium-sized catchments in Ontario (Bjerkelund and Ongley, 1980; Ongley *et al.*, 1981). The Bow and Oldman rivers, unlike their Ontario counterparts, do not display a multiplicity of competing land uses and are therefore relatively simple, albeit large, fluvial systems within which to carry out long-distance pathway research.

The objectives are (1) to identify biogeochemical pathways of phosphorus, heavy metals and organochlorine compounds in water, suspended sediments and aquatic plants; (2) to define pathway characteristics in terms of discharge regimes typical of prairie rivers; (3) to define pathways, taking into account time-of-travel, seasonality of point and diffuse sources, and potential riverine sinks; (4) to define spatial and seasonal variations of the chemical forms, and their relationships with hydrophysical characteristics and with the conventional measures of "total" and filterable chemical forms; and (5) to evaluate pathway information in the context of efficiency of conventional monitoring information for identifying patterns and causality of nutrient and contaminant stress in the aquatic ecosystem. This report consolidates and summarizes observations reported in detail in Blachford (1982) and Ongley and Blachford (1982a,b).

## **STUDY AREA**

The Bow and Oldman rivers rise in the Rocky Mountains and flow across the plains of southern Alberta. They merge in southeastern Alberta to form the South Saskatchewan River, a major interprovincial river in western Canada which flows eventually to Hudson Bay.

The study focusses primarily upon the reach of river extending downstream from Calgary on the Bow and from Lethbridge on the Oldman to their confluence at Bow

Island. This represents river distances of 366 and 155 km, respectively (Fig. 1, Tables 1 and 2). The Bow and Oldman each have one major point source: Calgary and Lethbridge, respectively. Diffuse sources in these rural basins are limited to irrigation return flows and occasional riparian feedlots. Major tributaries are Highwood River and Arrowwood Creek on the Bow and Little Bow River flowing into the Oldman.

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 in 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 area there are no significant settling environments. Carseland Dam is in reality a large weir without significant storage, and Bassano Dam has been almost completely silted in for many years.

Predominant bedrock formations in the studied portion of both basins are shallow marine deposits of semiconsolidated sandstones and shales with considerable unconsolidated clay. The unconsolidated banks of the river valleys provide an inexhaustible source of fine-grained sediment. The salt content of these brackish water deposits significantly affects irrigation return flow quality which, in turn, contributes significantly to the salt content of receiving rivers (Environmental Council of Alberta, 1982).

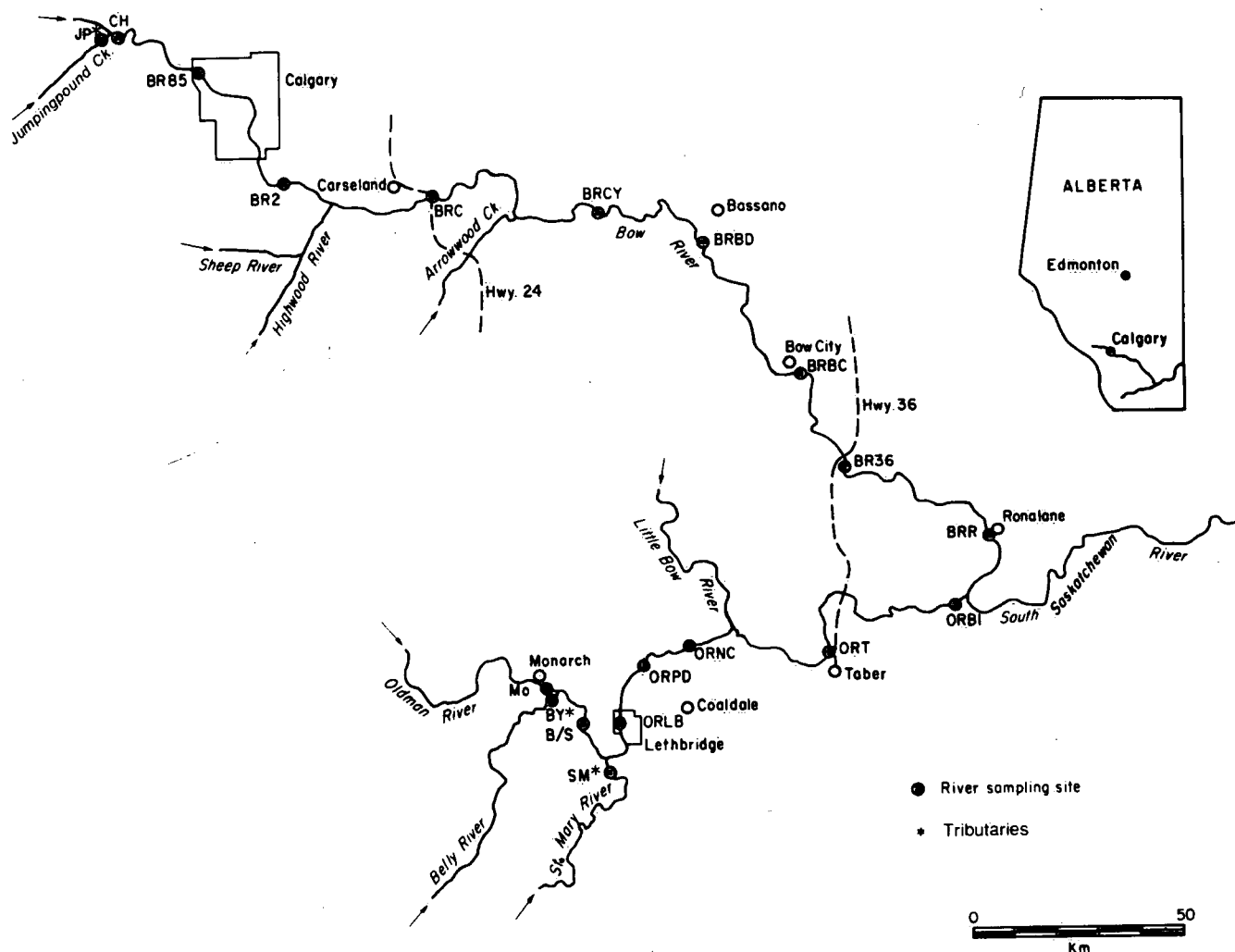


Figure 1. River sites on the Bow and Oldman rivers, southern Alberta.



Table 1. River Sampling Sites and Dates

Site	Field code	June 1980	July-August 1980	September-October 1980	May 1981
<b>Bow River</b>					
Upstream from Calgary: 85th St. Bridge	BR85	80-06-26	80-07-29	80-10-03	81-05-25
Downstream from Calgary STPs (Steer's Ranch)	BR2	80-06-27	80-07-30	80-10-04	81-05-26
Below Carseland Weir at Hwy. 24	BRC	80-06-28	80-07-31	80-10-05	81-05-27
Bow River near Cluny at Hwy. 842	BRCY	80-06-28	80-08-01	80-10-06	81-05-28
Bow River below Bassano Dam	BRBD	80-06-29	80-08-02	80-10-07	81-05-29
Bow River at Bow City (Hwy. 539)	BRBC	80-06-29	80-08-04	80-10-09	81-05-30
Bow River at Hwy. 36	BR36	80-06-30	80-08-05	80-10-10	81-05-30
Bow River at Ronalane Wasteway (Hwy. 524)	BRR	80-06-30	80-08-06	80-10-11	81-05-31
<b>Oldman River</b>					
At Lethbridge, Hwy. 3	ORLB	80-06-22	80-08-13	80-09-26	81-05-19
Downstream from Lethbridge, near Piyami Drain	ORPD	80-06-23	80-08-14	80-09-27	81-05-20
Highway 845 near Coaldale	ORNC	80-06-23	80-08-15	80-09-28	81-05-21
Highway 864 near Taber	ORT	80-06-24	80-08-16	80-09-29	81-05-21
Upstream from South Saskatchewan River at Grand Forks	ORBI	80-06-24	80-08-18	80-10-01	81-05-22
<b>Auxiliary river sites: Oldman River</b>					
Oldman River below Monarch (downstream from Hwy. 3)	Mo	80-06-22			
Belly River above confluence	BY*	80-06-22			
Oldman River between Belly and St. Mary rivers	B/S	80-06-22			
St. Mary River above confluence	SM*	80-06-22			
Jumpingpound Creek	JP*				81-05-24
Bow River at Cochrane	CH				81-05-24

\*Sample at mouth of tributary to Oldman River.

Table 2. Distances (km) between River Sampling Sites

Site	Distance	Cumulative distance
<b>Bow River</b>		
BR85	0	0
BR2	43.1	43.1
BRC	47.8	90.9
BRCY	77.0	167.9
BRBD	46.3	214.2
BRBC	60.3	274.5
BR36	31.5	306.0
BRR	59.6	365.6
<b>Oldman River</b>		
Mo	0	0
BY*	9.2	9.2
SM*	32.2	41.4
ORLB	14.3	55.7
ORPD	25.5	81.2
ORNC	17.9	99.1
ORT	42.9	142.0
ORBI	68.8	210.8

\*Confluence with Oldman River.

Source: Report on Determination of River Distances for the Saskatchewan-Nelson River Basin. 1980. PFRA Hydrology Report No. 95.

Although the dry plains climate does not directly affect water quality, it has an important indirect effect insofar as the large, irrigated areas of southern Alberta require large extractions of water from both rivers—principally at Carseland and Bassano on the Bow, at Bocket on the Oldman and from the St. Mary and Belly rivers (tributaries to the Oldman, Fig. 1). Although there are no known bedrock aquifers in the region which impinge on the two rivers, limited surface aquifers are contained in the Pleistocene deposits of the Oldman River valley and the upper half of the studied portion of the Bow River valley (Canada West Foundation, 1982). In the case of the Oldman River, surficial groundwater plays no role in the hydrologic regime between Lethbridge and the mouth of the Oldman River (Water Survey of Canada, personal communication).

## METHODS

### Site Selection and Sampling Strategy

The selection of river sampling sites involved consideration of point and diffuse sources, potential riverine sinks and accessibility. Because the program focusses upon the downstream 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 from urban impact (BR85 and ORLB; Fig. 1, Table 1). Downstream sites (primary sites, Fig. 1) were chosen at approximately equidistant intervals. The distances between sites were determined on the basis of logistics and earlier experience with downstream geochemical differentiation (Ongley *et al.*, 1981).

Major sources to the Bow River below Calgary are the Highwood River and Arrowwood Creek (Fig. 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 (Fig. 1) were added to the June 1980 sampling run of the Oldman River 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 those rivers contribute major sediment loadings to the Oldman River system. Additional sites were added to the spring 1981 sampling run on the Bow River to obtain a secondary baseline site for the Bow (CH) and to characterize the geochemical contribution from Jumpingpound Creek (JP\*) at a time when it was a major contributor of suspended sediment to the Bow upstream from Calgary.

The effects of seasonality upon chemical characteristics of solutes, solids and aquatic plants were evaluated by sampling during seasonal discharge regimes typical of prairie rivers. Figure 2 illustrates the relative position of each sampling run on the annual hydrographs. Sampling was carried out in early summer (June), summer (July-August) and fall (September-October) 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 upon the discharge effects of alpine snowpack melt. Sampling in spring of 1981 coincided with peak flows owing to foothill snowpack melt and considerable rainfall across southern Alberta. The summer (1980) run in the lower Bow was conducted at a time of fluctuating water levels due to extractions for irrigation and frequent rainfall. The fall (1980) run represented very stable hydrologic conditions.

The river sites were sampled sequentially downstream, representing the closest approximation to time-of-travel

(hydrologic synoptic sampling) possible with the sampling equipment employed. Suspended sediment data for each of the primary sites represent a time-integrated sample of from 0.3 h for the spring of 1981 to more than 6 h for the summer and fall of 1980. The variation of sampling time reflects in-stream concentrations of suspended sediment.

A selection of irrigation return flows in the study area were sampled in a concurrent study from June to September 1980. Water and suspended sediment were analyzed for metals and phosphorus. The geochemical contribution of the return flows to the Bow and Oldman rivers is described by Joseph and Ongley (in preparation).

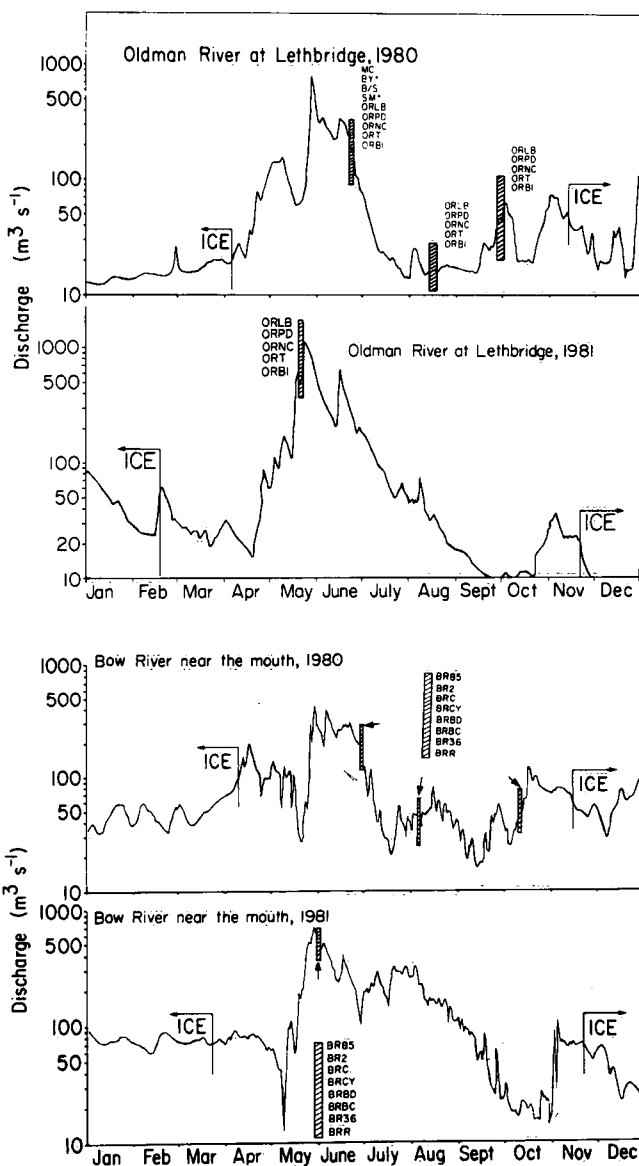


Figure 2. Discharge hydrograph for Bow River near the mouth and Oldman River at Lethbridge, 1980-1981. Sampling periods for the indicated sites are shown. Water Survey of Canada.

## Water

Water samples were collected at the primary sites during each of the discharge regimes and at the auxiliary sites as noted above. Water samples for metal analysis (Fe, Mn, Ni, Pb, Zn, Co, Cd, Cu, Cr) were collected in pretreated Nalgene polypropylene bottles near the surface of each section at 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. Filtration was carried out in the field, initially using borosilicate glass funnels, then Sartorius polystyrene filtering funnels. Filtration was through a Gelman glass-fibre filter (to remove coarse sediment) placed on a Millipore 0.45- $\mu$ m 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°C.

Water for metal analysis was concentrated tenfold, digested with hot concentrated  $\text{HNO}_3$ , leached with 10% HCl, then analyzed by flame atomic absorption spectrophotometry with 10% replication plus blanks. Several replicates of total and filtered water were taken during the field program. Distilled water carried for field use was sampled at each site as a check for potential contamination.

Water samples for phosphorus, total mercury and organic contaminants were collected as close to midstream as possible. Pretreated bottles for phosphorus and mercury were supplied by Alberta Environment and the Freshwater Institute, respectively. Raw water for organic contaminant analysis was collected directly in 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 5 min following sample collection. This procedure, reflecting the experience of the Pesticide Laboratories of the Ontario Ministry of Environment and the Ontario Research Foundation, enhances preservation of organic contaminants in samples which, in this study, had to be stored at 4°C for several weeks prior to analysis.

Total-P and total dissolved-P in water were collected in duplicate at each site and were determined by Alberta Environment using standard methods. Total mercury was analyzed at the National Water Research Institute, Winnipeg; during one complete season (spring, 1981) it 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. All of the methods, including discussion of accuracy and precision, are found in Blachford (1982).

## Sediments

Suspended sediments were collected at primary sites in early summer, summer, fall and spring and at the auxiliary sites in early summer. Bulk samples of suspended sediment were quantitatively recovered in the field with an Envirodata Sedisamp continuous-flow centrifuge system (Ongley and Blachford, 1982b). As noted above, these samples represent a time integration of from 0.3 h to more than 6 h, depending upon the suspended sediment concentration. Centrifuged samples were pumped from just under the water surface to avoid floating debris and within the main flow of the river, usually one quarter to one third of the channel width away from one of the banks. Sampled sites were well downstream from point sources or tributary inputs to ensure complete mixing across the section. 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. This sampling strategy, described by Ongley and Blachford (1982b), minimizes sand collection while ensuring representative recovery of the silt-clay (geochemically active) fraction which is known to be equally distributed in the vertical section (Ongley, 1982b).

Field-centrifuged samples were transferred as a slurry to pretreated 500-mL Nalgene bottles, held at 4°C for up to 24 h, then bench-centrifuged to recover the solids. The solid material was immediately 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 immediately frozen.

Sediment concentrations were approximated by two methods. One 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- $\mu$ m filter. The sediment concentrations used in this study are those found by the first method. Errors in this method are probably commensurate with errors inherent in gravimetric procedures, especially for low values of concentration. The first method produces a time-integrated average, whereas the latter is an instantaneous estimate.

Organic content of suspended sediment was estimated by loss on ignition in small subsamples. Sediments were

oven-dried at 105°C, then heated for 1 h at 550°C (Dean, 1974). Particle size analysis of the sediments was performed using a Micromeritics Sedigraph 5000D. Samples were stirred for approximately 1 h using a 5% Calgon solution to ensure complete dispersion. Results are expressed as "equivalent settling diameter."

Limited quantities of suspended sediment prohibited the use of sequential extraction techniques (Gibbs, 1977; Tessier *et al.*, 1979). All suspended sediments were analyzed for metals, using a hot concentrated HNO<sub>3</sub> acid – 10% HCl digestion and flame atomic absorption spectrophotometry. This method indicates the amount of total metal present in the sample with the exception of metals bound in the silicate lattice of clay minerals. Measured concentrations of metals were prorated onto the silt-clay fraction of the sample following particle size analysis. As for water, chemical analysis of sediments utilized a 10% replicate rate, plus blanks and appropriate standards.

Phosphorus fractionation on suspended sediment was performed using the Williams *et al.* (1976) method and as detailed in Mayer and Williams (1981). Each sample is partitioned into two subsamples; the first is analyzed for apatite phosphorus (A-P) and non-apatite phosphorus (NAI-P); total-P (T-P) and organic-P (O-P) are determined from the second. Apatite phosphorus is the orthophosphate that is present in crystal lattices of apatite grains, whereas NAI-P consists of all remaining orthophosphate ions in the sediment sample. Organic phosphorus includes all phosphorus linked to carbon atoms by C-O-P or C-P bonds (Williams *et al.*, 1976).

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

A selection of bank samples was collected during the spring of 1981, 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

Aquatic macrophytes found in greatest abundance in the Bow River over the 1980 growing season were *Potamogeton* sp. *Potamogeton vaginatus* accounted for

most of the biomass downstream from Calgary; *P. filiformis* and *P. crispus* were also observed. The macrophyte samples were often a composite of species and were identified only to the genus level. *Potamogeton* sp. as well as filamentous algae were collected in the Oldman River.

Whether or not macrophytes absorb nutrients through the roots and/or submerged shoots (Carignan and Kalff, 1980; Carignan, 1982) appears to be irrelevant here. The very coarse-grained substrate, while creating an adequate rooting environment, appears to provide little sediment-related nutrition for root uptake, an observation also made by Wong and Clark (1976) in their study of Ontario rivers. Bioavailable nutrients and metals are largely associated with the aqueous medium as measured in the water column. Uptake through roots probably reflects mainly solutes in river water as they pass through the coarse substrate under hydraulic forces. Concentrations of phosphorus, metals and other contaminants in plants, therefore, should largely reflect availability of metals in the water phase rather than a reservoir of labile material in bottom sediments.

A representative collection of biomass was taken at all primary river sites during the summer and fall runs to reflect the major period of productivity. Macrophytes (entire plants including roots) and attached filamentous algae were collected across each river site and over a reach of up to 2 km where plants were 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. Plant materials were ground to a powder in a Wiley mill and analyzed for metals, phosphorus, and organochlorine compounds using the same methods as for suspended sediment.

The Williams *et al.* (1976) fractionation scheme, which was designed for sediments, introduces certain inconsistencies for plant-related phosphorus values. Experimental work by Painter (personal communication) indicates that significant tissue phosphorus is extracted by the A-P and NAI-P digestions and that O-P, which measures humic-associated phosphorus in sediment, is inappropriate for tissue-P in plant material. Although we have used the Williams technique on all sediment and plant samples (mainly for consistency in dealing with suspended sediments, which vary from highly mineral to highly organic), Painter's work on cultured samples indicates that the total-P value most closely represents tissue-P. For reasons noted below, we use NAI-P + O-P to approximate tissue-P.

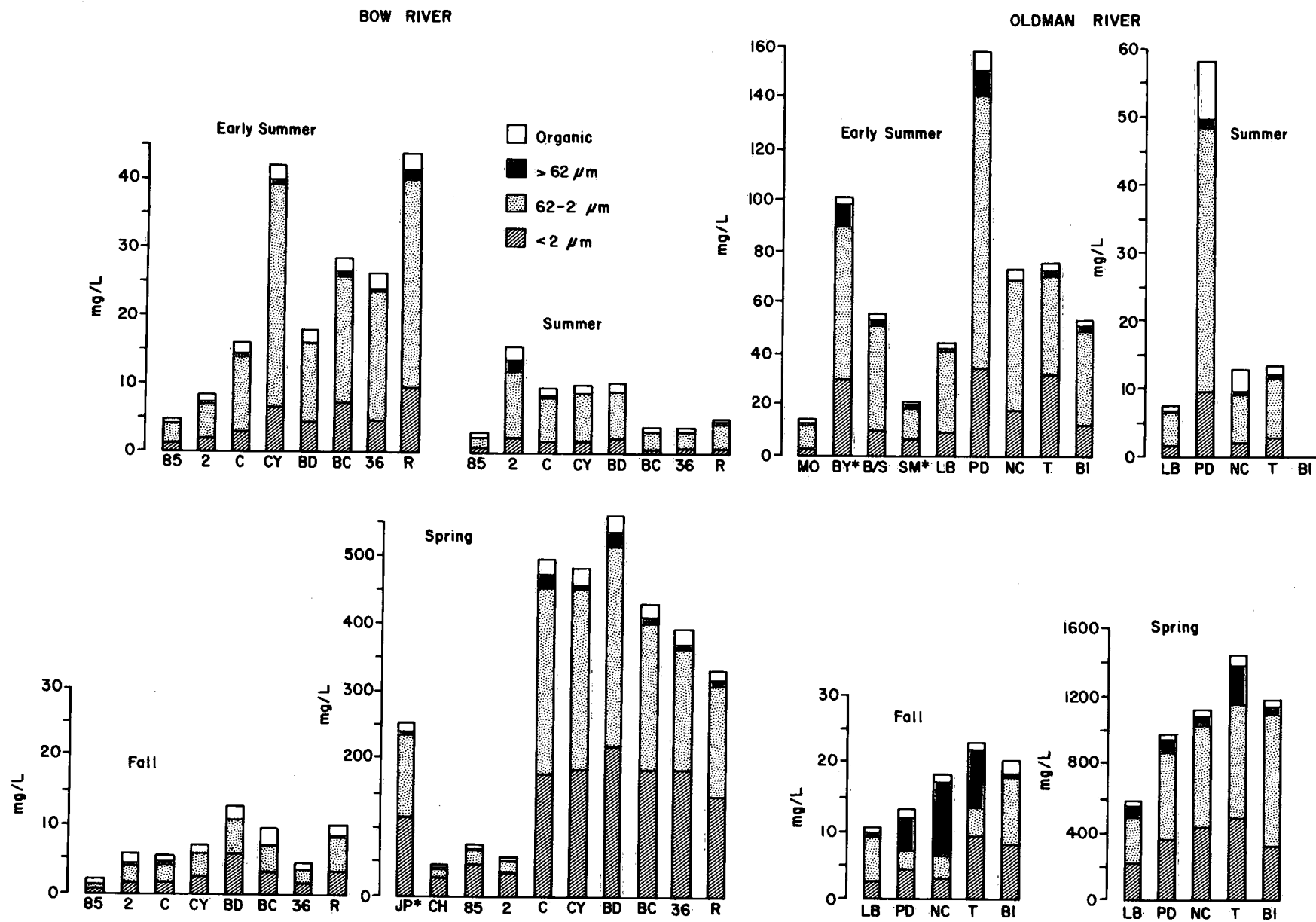


Figure 3. Suspended sediment concentrations and organic/mineral fractions of the sediments. The height of each bar represents the total sediment concentration. The organic component and the sand (> 62  $\mu$ m), silt (62-2  $\mu$ m) and clay (< 2  $\mu$ m) components of the mineral material are indicated as proportions of the total sediment concentration.

## Data Reliability

It is well known that single samples are not a reliable estimate of ambient water chemistry. In this study it was not feasible to take large numbers of samples at each site to determine site variance. However, all water samples were taken in duplicate, suspended sediment data were generated from time integrated bulk samples, and plants (roots, stems, shoots) were collected from several locations at each sampled section. As noted above, analysis included field blanks (for contamination) and a minimum 10% replication as well as laboratory blanks (Blachford, 1982). Although the data may not be statistically representative of seasonal conditions, the large differences observed both in time and space indicate that the data are characteristic of biogeochemical conditions within the flow regime represented in each sampling run.

The degree to which our phosphorus (in water) data are characteristic of seasonal conditions can be evaluated with independent data taken at two sites on each of the Bow and Oldman rivers by the Water Quality Branch of Environment Canada. Although not collected on the same dates, these monthly data indicate that our values are typical of values for that period. Moreover, certain seasonal trends are also apparent in the monthly data sets. We conclude that the trends noted below are indicative of the conditions under which the samples were taken and that they generally represent a set of conditions occurring during the season under investigation.

## RESULTS AND DISCUSSION

### 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. For geochemical purposes it is the  $<62\text{-}\mu\text{m}$  fraction which is of significance due to large surface area, especially for clay-size ( $<2\text{ }\mu\text{m}$ ) and colloidal materials. The organic content of suspended sediment may be a quantitatively significant component of the particulate load during periods of major biomass production because of the strong adsorptive properties displayed by organic colloids.

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 3. The heights of the bars in each histogram correspond to sediment concentration; the size fractions represented within each bar are the proportions by weight, of each particle size category. Seasonality of the silt-clay and organic content is highlighted in Figure 4.

Sediment in the Bow River shows changes in particle size composition over the year from predominantly silt-size ( $62\text{-}2\text{ }\mu\text{m}$ ) particles with some clay in early summer, to a marked increase in clay content in fall. An increased proportion of organic solids in summer and fall reflects the period of major biomass production. Spring samples have similar quantities of silt and clay with small amounts of sand and organic matter. The sediment concentration in the spring ( $\pm 500\text{ mg/L}$ ) is an order of magnitude greater than that in any other season. Early summer concentrations are less than  $45\text{ mg/L}$ ; summer and fall concentrations are less than  $15\text{ mg/L}$ .

Sediments in the Oldman River have a high silt content in early summer and an increased organic content in summer and fall. The proportion of clay increases in fall and 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

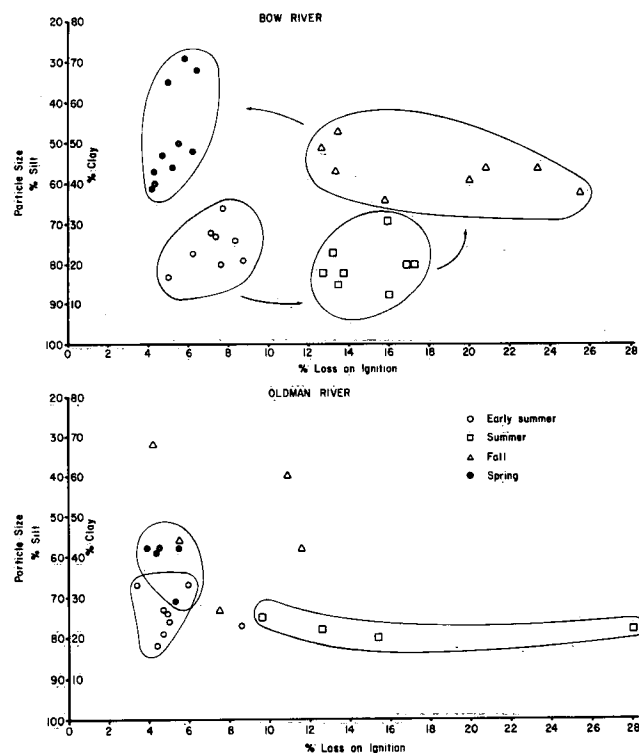


Figure 4. Seasonality of particle size and organic content of suspended sediments. The silt/clay ratio is calculated from the portion of mineral sediment  $<62\text{ }\mu\text{m}$ . Organic content determination by percent loss on ignition. Data are for all sites.

order greater than those in the summer and fall. As for the Bow River, high spring and early summer sediment concentrations exert a strong influence on river chemistry.

## Phosphorus

Phosphorus concentrations in water and suspended sediments in the Bow and Oldman rivers are presented in Figures 5 and 6. The diagrams are arranged to show the order in which sampling occurred: early summer, summer, fall 1980 and spring 1981. Two estimates for total-P on sediments are given: the summation of the individual phosphorus fractions and an independent determination of total-P (open bar). The difference in these two values is an indication of analytical variance.

### *Water*

Phosphorus in Bow and Oldman River water (Fig. 5) shows variation in total concentration, particulate and dissolved proportions and downstream trends among the seasons. Water in spring contains greater concentrations of total phosphorus than in other seasons, reflecting diffuse source runoff from large contributing areas of the basin. The phosphorus load is largely (>90%) in particulate form, due to the high concentration of suspended sediment during 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, probably due to a reduction in diffuse source contribution and lower sediment concentrations. Substantially less phosphorus is in particulate form in the Bow River. The higher proportion of total phosphorus in the particulate fraction in the Oldman compared to the Bow is a function of the relatively higher suspended sediment concentration and the lesser impact of dissolved phosphorus contribution from Lethbridge to the Oldman than from Calgary to the Bow. Below urban areas dissolved concentrations increase as the total volume of flow is reduced.

Summer and fall waters have slightly higher total phosphorus concentrations than in early summer. The reduced flow conditions and sediment concentrations result in a greater proportion of the total phosphorus falling in the dissolved phase with reduced amounts in particulate form at upstream sites. Farther downstream in the Bow, independent monthly data indicate that TDP is depleted throughout the summer and fall, suggesting that summer and fall biomass exert at least as much influence on TDP (and TP) levels as discharge during major growth periods. The elevated levels of total phosphorus

at BRBD, BRBC and BRR in the summer may have resulted from local rainstorm events during the sampling run and fluctuating water levels on account of irrigation extractions at Bassano Dam. These changes in flow did not affect dissolved phosphorus concentrations but resulted in a disproportionate particulate contribution to total phosphorus. High dissolved phosphorus levels at ORPD and ORNC reflect sources from Lethbridge and very reduced sediment concentrations. The low TP levels at ORT and ORBI appear suspect.

The fall samples were collected during a stable flow regime. Total and dissolved phosphorus concentrations decline steadily from BR2 to BRR and from ORPD to ORBI. The downstream trend of declining total and dissolved phosphorus with increasing proportion of particulate phosphorus indicates a net loss in the downstream direction and conversion from one form to the other. This is likely occurring through the combined effect of biological uptake by macrophytes and benthic algae, and sorption of soluble orthophosphate ions onto mineral and organic surfaces with precipitation of the ions to form compounds of low solubility. In view of a similar decline in soluble phosphorus in the Bow River during summer, similar mechanisms may be assumed to occur during the entire low-flow period.

### *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 in the Bow and Oldman rivers (Fig. 6). The exception is BR2 where a larger portion of the phosphorus is NAI-P, presumably reflecting the influence of the Calgary sewage treatment plant (STP). Apatite-P, a non-enriched background mineral phosphate produced from eroding prairie soils, dominates at all sites in fairly constant proportions. Phosphorus speciation of bank materials collected at BRBD, BRBC, ORPD and ORBI is almost identical with that found at a non-enriched site (e.g. CH, Fig. 1). The low total-P concentrations in the spring reflect the large sediment loads with 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 indicates decreasing amounts of NAI-P and O-P.

Early summer sediments contain an increased amount of O-P and NAI-P and a much reduced proportion of A-P. Phosphorus concentrations are higher than in the spring due to point source enrichment and a reduced quantity of sediment in transport. The influence of Lethbridge is noted by the NAI-P and O-P concentration increases below the point source.

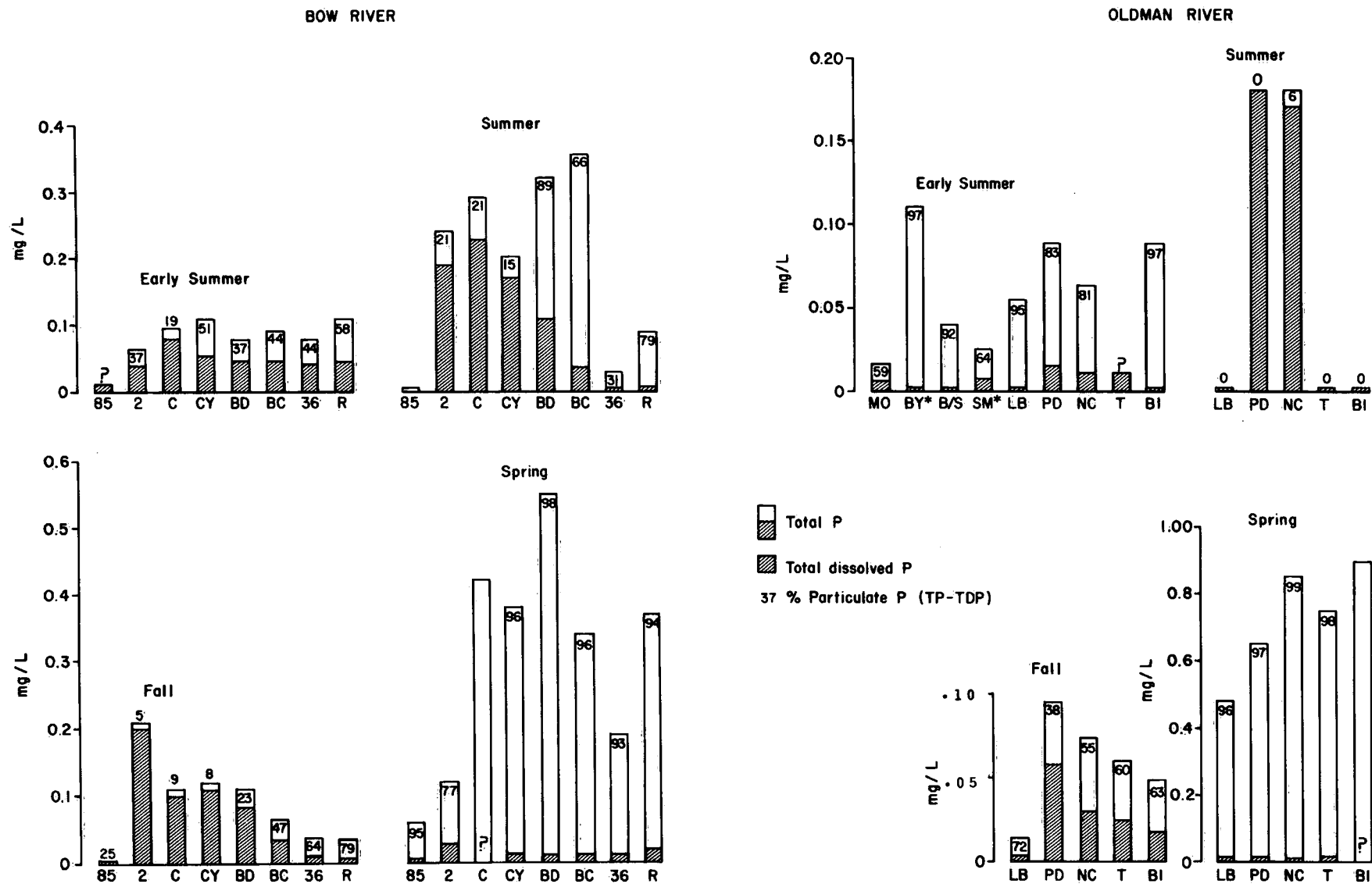


Figure 5. Total and dissolved phosphorus concentrations in water. The particulate fraction is calculated as the difference between total and dissolved phosphorus. Particulate phosphorus is presented numerically on a percentage of total-P. Missing fractions are denoted by "?".



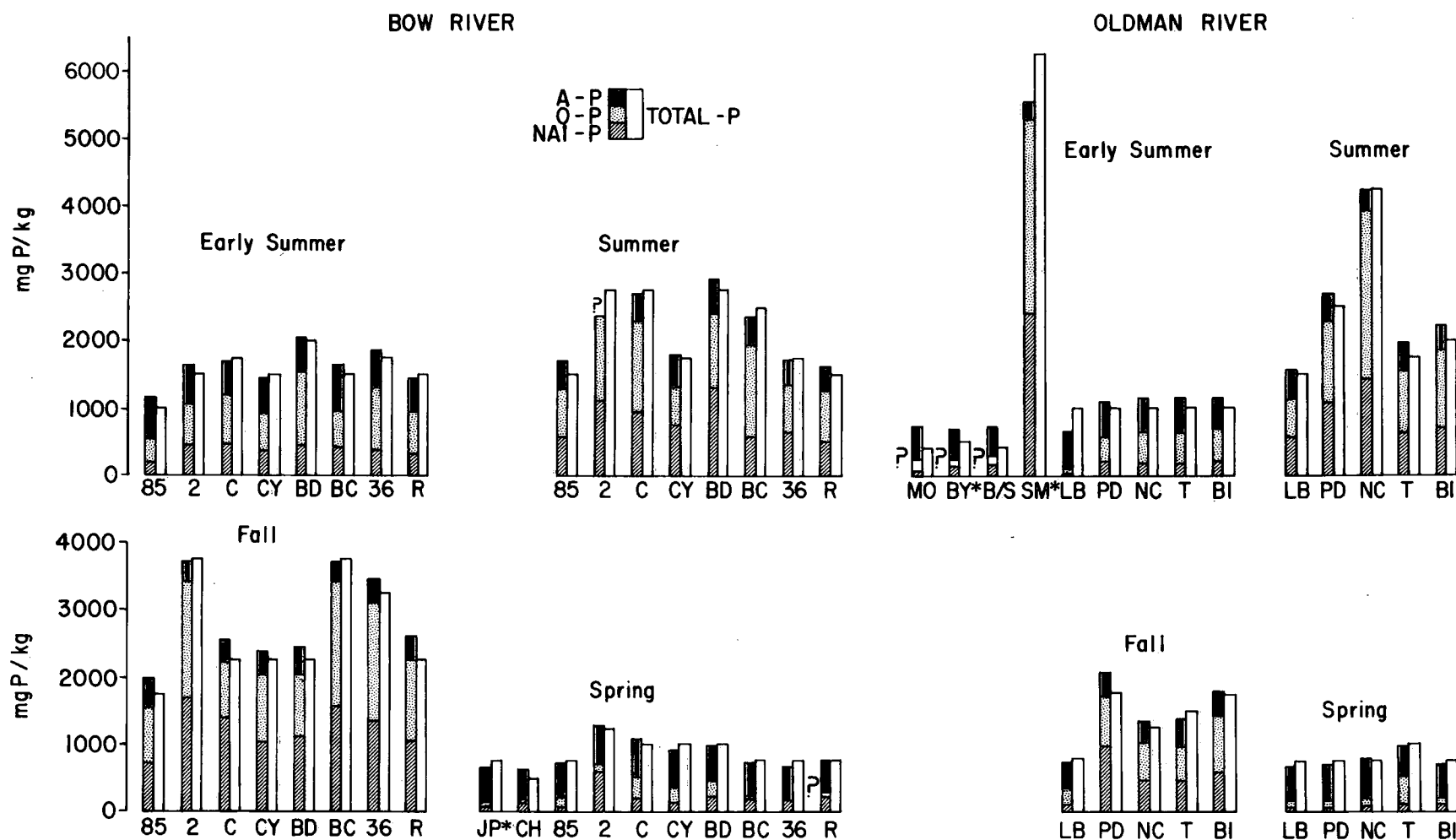


Figure 6. Phosphorus speciation on suspended sediments. The amount of each phosphorus species can be calculated using the ordinate axis scale. The sum of the three species cannot be computed where one of the fractions is missing (denoted by "?"). Difference between TP and the sum of NAI-P, O-P and A-P is a measure of analytic imprecision.

Summer and fall sediments are further enriched as sediment concentrations decline. The trends in total-P in summer and especially in fall follow very closely the trends in organic content of the sediments. Organic solids may be contributed to the suspended sediment load upstream from the Calgary STP, and from decaying populations of benthic algae and macrophytes along the course of the river.

While the proportion of A-P increases, total-P decreases in summer and fall from BR2 to BRCY, likely as a result of the dilution of enriched sediment observed at BR2 by tributaries farther downstream carrying background levels of phosphorus in apatite form. This deduction is consistent with observations of reduction of both metal concentrations and organic content of sediments at the same sites.

#### *Aquatic Plant-related Phosphorus*

Phosphorus concentrations in aquatic macrophytes and filamentous algae are presented in Figure 7 for the

Bow and Oldman rivers. Although the plants were rinsed in river water prior to drying, the plant samples contained observable quantities of enmeshed mineral sediment and calcium precipitates. Painter (personal communication) indicates that tissue-P is extracted by A-P and NAI-P digestions; however, because the A-P fraction is generally low relative to NAI-P and O-P and because of observed enmeshed mineral sediments, we here equate tissue-P with the sum of NAI-P + O-P. This is probably a reasonable assumption, as A-P was only 1% of the NAI-P + O-P value in Painter's cultured samples.

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.

Concentration of phosphorus in plant tissue is known to be related to the amount of available phosphorus in the surrounding water and rooting environment (Gerloff and Krumbholz, 1966; Wong and Clark, 1976). The relationship

Table 3. Enrichment Ratios of Phosphorus in Plants

Season	Site	NAI-P + O-P (mg/kg)	TDP (mg/L)	Enrichment ratio* (NAI-P + O-P/TDP)
Summer	Bow River			
	BR85	2542	<0.005	$> 5.1 \times 10^5$
	BR2	3128	0.19	$1.6 \times 10^4$
	BRC	3110	0.23	$1.4 \times 10^4$
	BRCY	3440	0.17	$2.0 \times 10^4$
	BRBD	2984	0.11	$2.7 \times 10^4$
	BRBC	2623	0.039	$6.7 \times 10^4$
	BR36	3541	0.017	$2.1 \times 10^5$
Fall	BRR	2283	0.019	$1.2 \times 10^5$
	BR85	1690	<0.003	$> 5.6 \times 10^5$
	BR2	3467	0.20	$1.7 \times 10^4$
	BRC	3033	0.10	$3.0 \times 10^4$
	BRCY	1693	0.11	$1.5 \times 10^4$
	BRBD	2966	0.085	$3.5 \times 10^4$
	BRBC	2253	0.035	$6.4 \times 10^4$
	BR36	1727	0.013	$1.3 \times 10^5$
Summer	BRR	1893†	0.007	$2.7 \times 10^5$ †
	Oldman River			
	LB	1900	<0.003	$> 6.3 \times 10^5$
	ORPD	3022	0.17	$1.8 \times 10^4$
	ORNC	3375	0.016	$2.1 \times 10^5$
		4376†		$2.7 \times 10^5$
	ORT	2362	<0.003	$> 7.9 \times 10^5$
	ORBI	1480	<0.003	$> 4.9 \times 10^5$
Fall	LB	—	—	—
	ORPD	3930	0.059	$6.6 \times 10^4$
		3573†		$6.0 \times 10^4$
	ORNC	3241	0.033	$9.8 \times 10^4$
	ORT	2012	0.025	$8.0 \times 10^4$
		2328†		$9.3 \times 10^4$
	ORBI	2295	0.018	$1.3 \times 10^5$

\*Data from *Potamogeton* sp.

†Filamentous algae.

between plant and water phosphorus values is numerically expressed as an enrichment ratio in which plant-P is a ratio of available phosphorus in the water (Table 3). The spatial trends of the enrichment ratio and their management implications, discussed below, are subject to several caveats:

1. NAI-P + O-P is a reasonable estimate of tissue-P in plants;
2. Measurements of TDP are instantaneous values, whereas plant-P represents assimilation of phosphorus over a longer period; and

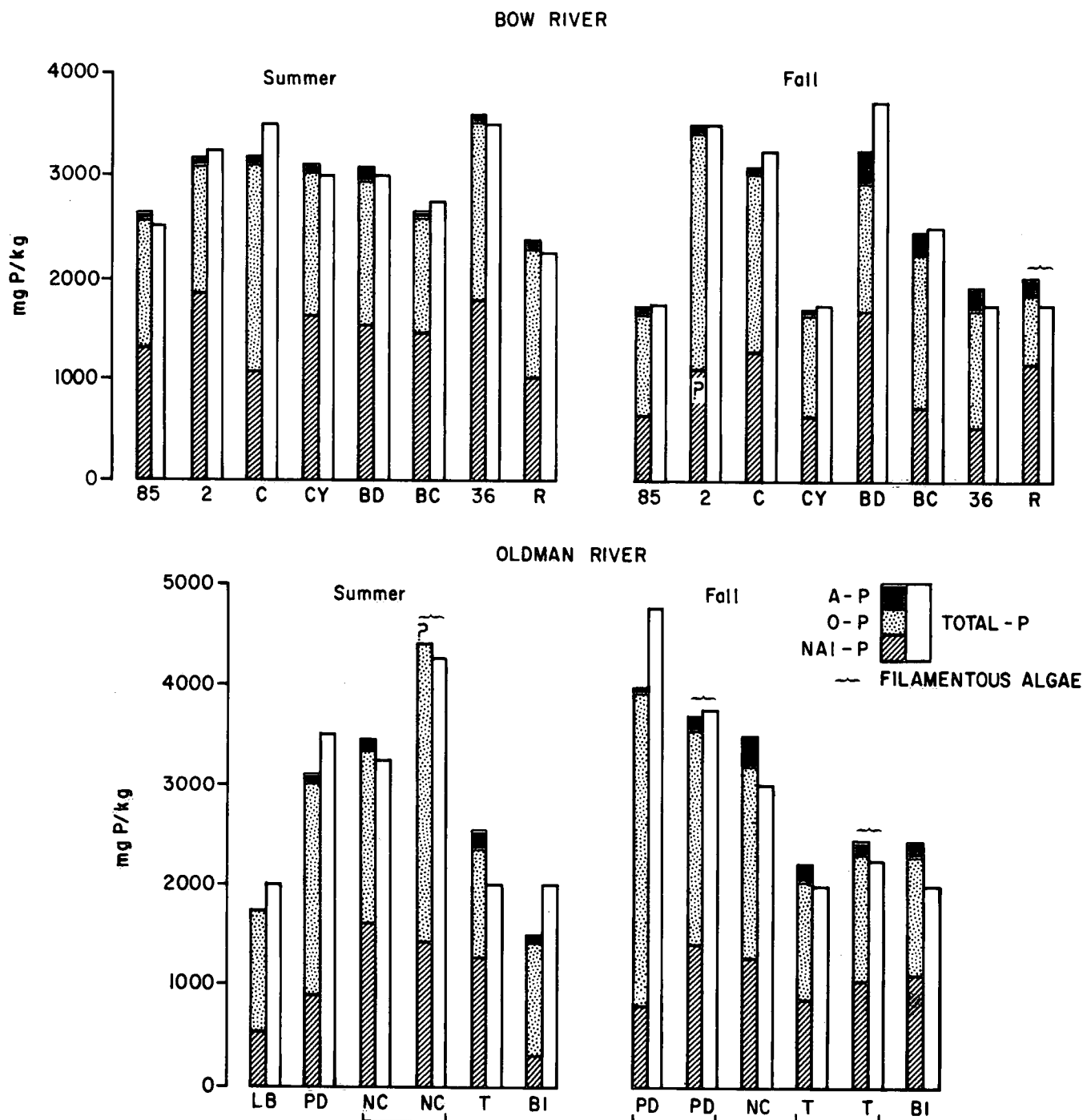


Figure 7. Phosphorus speciation in aquatic plants. Tissue-P is approximated by the sum of NAI-P + O-P. *Potamogeton* sp. are represented unless otherwise indicated. The symbol ( ) shows sites where macrophytes and algae are both represented.

3. TDP values are presumed to be characteristic of seasonal conditions. Comparable data collected independently by the Water Quality Branch of Environment Canada at several of our sites (both rivers) also support seasonal differentiation evident in our data. Generally, our values fall within independent data.

In both rivers there is an order of magnitude decline in TDP below the major sources of Calgary and Lethbridge, but only a relatively small reduction in plant-P. As a consequence the enrichment ratio increases dramatically downstream. These trends, plus the data from the unimpacted background site BR85, indicate that macrophytes and filamentous algae living in phosphorus-rich environments have lower enrichment ratios and only show a marked increase in phosphorus content close to the anthropogenic source. Plants in phosphorus-poor environments in these rivers display somewhat reduced levels of plant-P but have large enrichment ratios. Although the data are not entirely comparable, plant-P in phosphorus-poor reaches appears to be above threshold P levels established by Gerloff and Kromholz (1966) as growth-limiting for other *Potamogeton* species.

#### *Implications for Biomass Control*

The observation that large changes in TDP are reflected only by modest changes in plant-P suggests that measures of plant-P may not be useful indicators of nutrient stress. Stress may be more clearly reflected by density of the plant community within a reach. Elevated nutrient conditions appear to create favourable growth conditions in the Bow River. In comparison with the luxurious growth in the lower Bow in 1979, the impoverished growth in 1980 following spring floods of that year leads to the following hypothesis. The appearance and, probably, density of aquatic plants in the lower reaches of the Bow are mainly controlled by re-seeding of opportunistic species originating from areas of luxurious growth upstream. Once established, plant productivity is controlled by ambient levels of phosphorus. Measures of productivity and plant cover may be appropriate indicators of nutrient stress in an environment where equilibrium has been established between average nutrient conditions and population propagation. Where extreme perturbation in environmental conditions has occurred, such as the large flows that destroyed the dense plant community in the lower Bow in early 1980, the deduction of low potential productivity based solely 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 preceding spring.

Although nutrient conditions in the downstream reach are close to background (i.e. compared with 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 accumulate nutrients rapidly to levels in excess of their immediate requirements (luxury uptake) permits plants 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 luxurious plant growth in these years may well reflect the ability of plants to accumulate nutrients rapidly during brief periods of nutrient flux. If true, macrophyte control strategies would require, therefore, the suppression of brief nutrient pulses from point sources.

#### **Metals**

Concentrations of ten metals (Mn, Ni, Fe, Cu, Pb, Zn, Co, Cr, Cd, Hg) in water, suspended sediment and aquatic plants are presented in Figures 8a to 8j for the Bow and Oldman rivers. Seasonal and phase differences in concentration, downstream trends and comparisons between the rivers for each of the water, suspended sediment and plant phases are discussed.

#### *Water*

Most filterable and many total metals in the Bow and Oldman rivers are at concentrations below conventional detection limits. Many of the metals are detectable in total concentration in spring, whereas few are detectable in filterable form in any of the seasons. Spring metal levels tend to be approximately tenfold higher than concentrations in any other season.

The difference in metal concentrations between spring, on the one hand, and all other seasons is attributed to increased sediment concentration and a larger component of fine-grained material. Spring sediment concentrations are more than an order of magnitude larger than in other seasons and comprise a larger proportion of clay-size particles (Fig. 4). Physical characteristics also explain the downstream trends in metal concentrations. Sediment concentrations increase in spring from below 100 mg/L at upstream sites to more than 500 mg/L in the Bow and over 1400 mg/L in the Oldman at sites farther downstream, due to large inputs from several tributaries (especially Highwood River and Arrowwood Creek inputs to the Bow River) and from extensive bank collapse observed in both rivers.

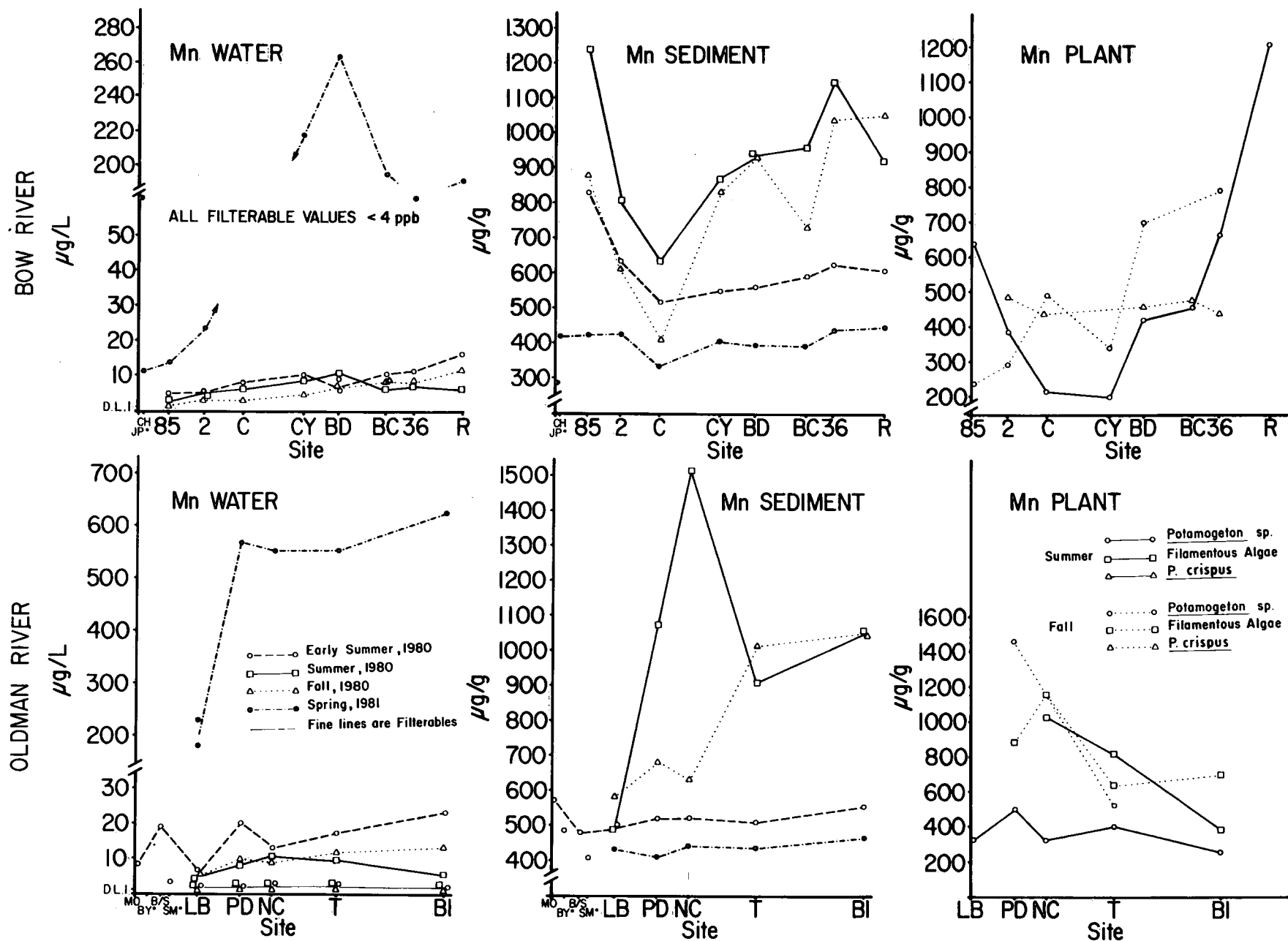


Figure 8a. Manganese concentrations in water, suspended sediment and plant phases for the Bow and Oldman rivers. Distance between sites on graphs is proportional to actual river distances.

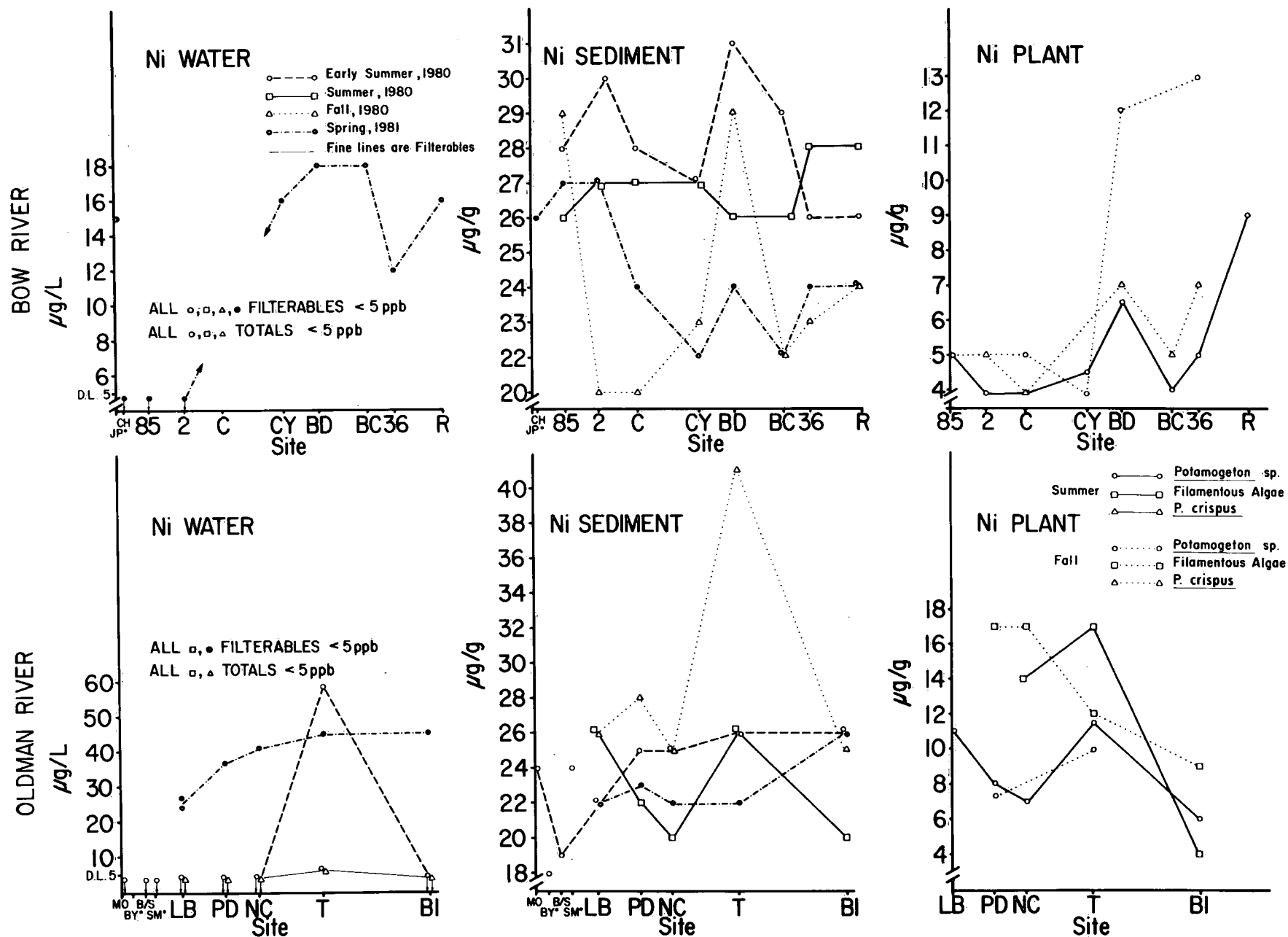


Figure 8b. Nickel concentrations in water, suspended sediment and plant phases for the Bow and Oldman rivers. Distance between sites on graphs is proportional to actual river distances.

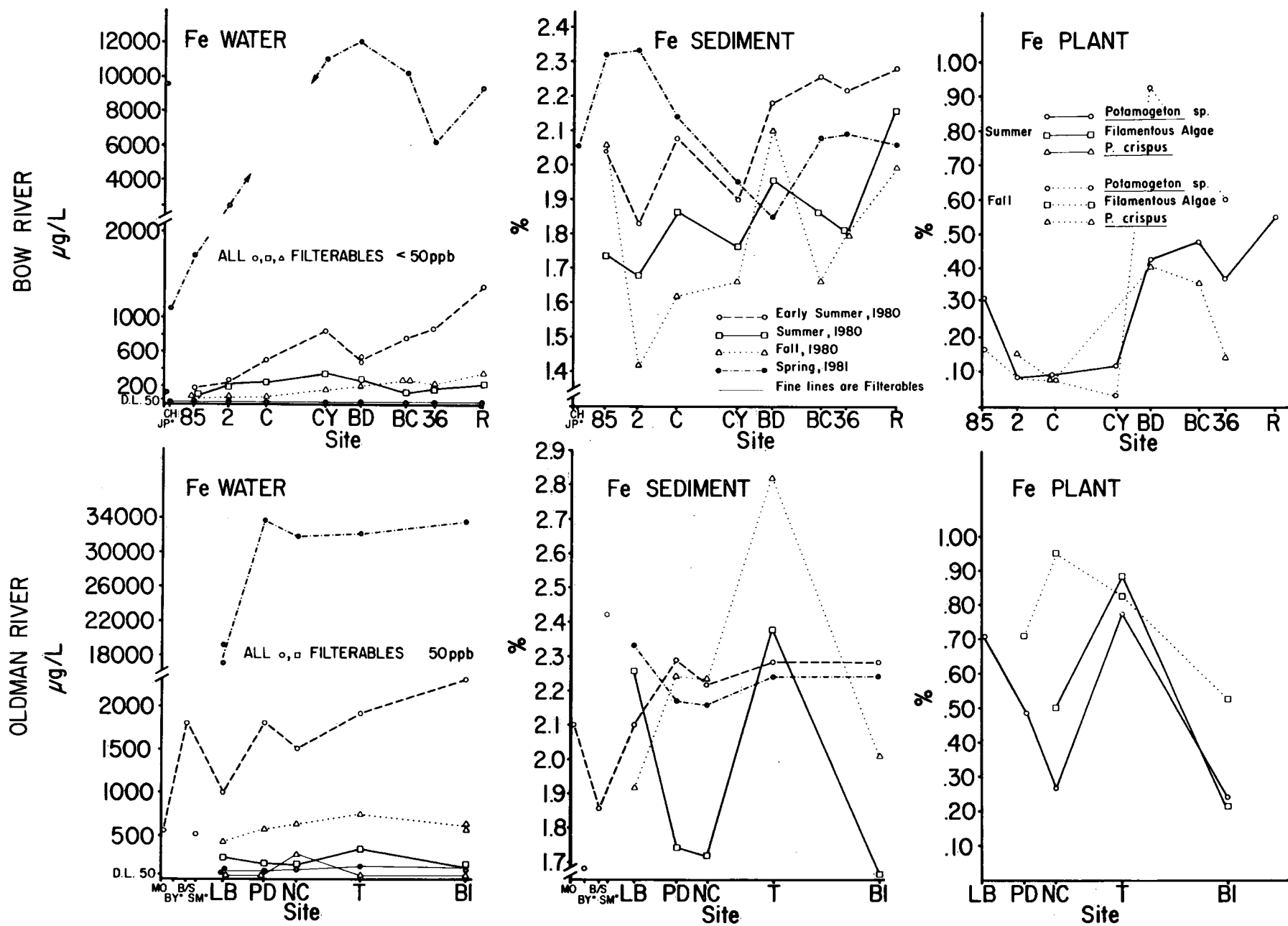


Figure 8c. Iron concentrations in water, suspended sediment and plant phases for the Bow and Oldman rivers. Distance between sites on graphs is proportional to actual river distances.

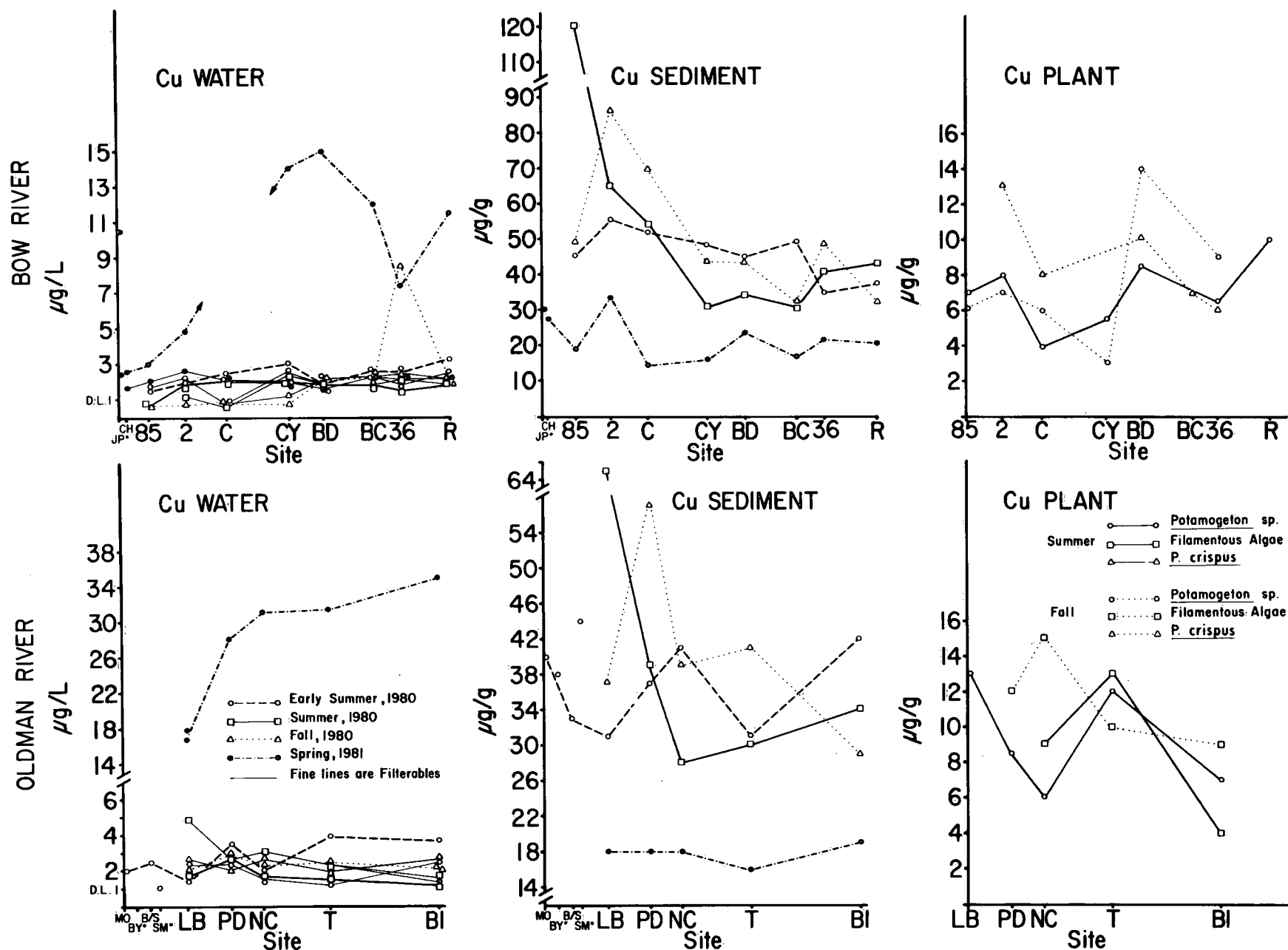
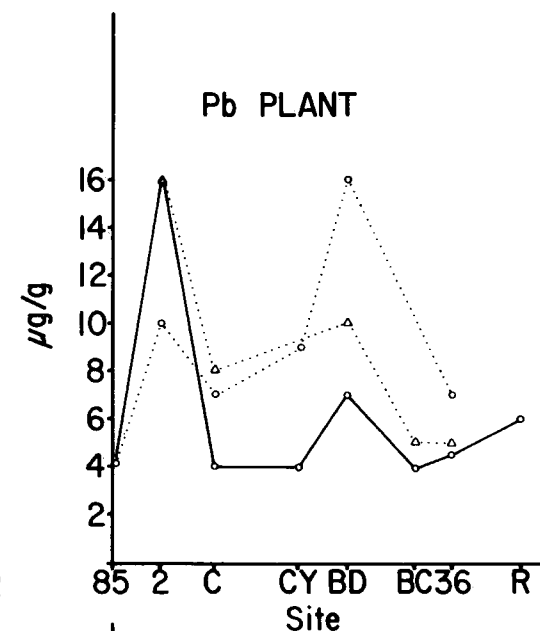
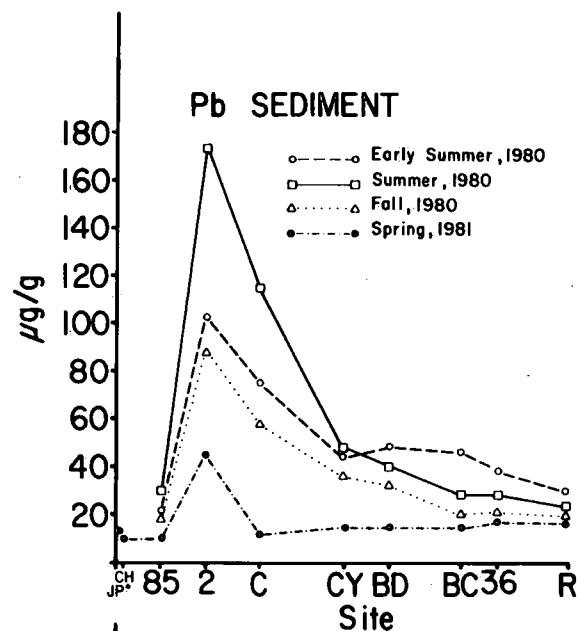


Figure 8d. Copper concentrations in water, suspended sediment and plant phases for the Bow and Oldman rivers. Distance between sites on graphs is proportional to actual river distances.



# BOW RIVER

ALL TOTALS AND FILTERABLES  
< DETECTION LIMIT



# OLDMAN RIVER

## Pb WATER

ALL ○, □, △, ● FILTERABLES < 10 ppb  
ALL ○, △ TOTALS < 10 ppb

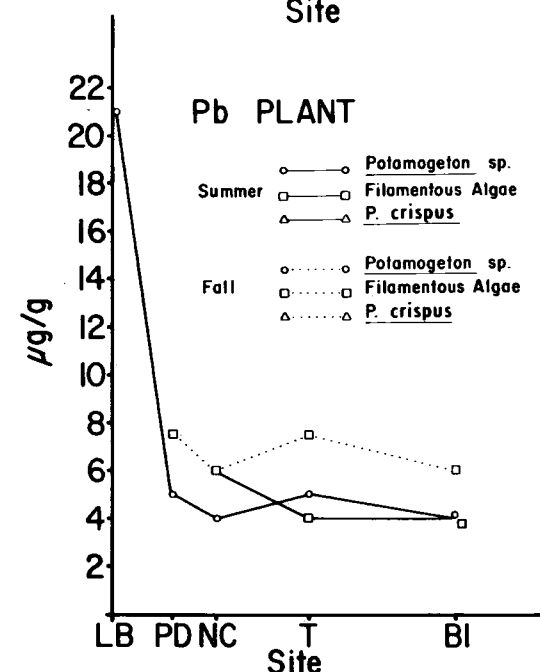
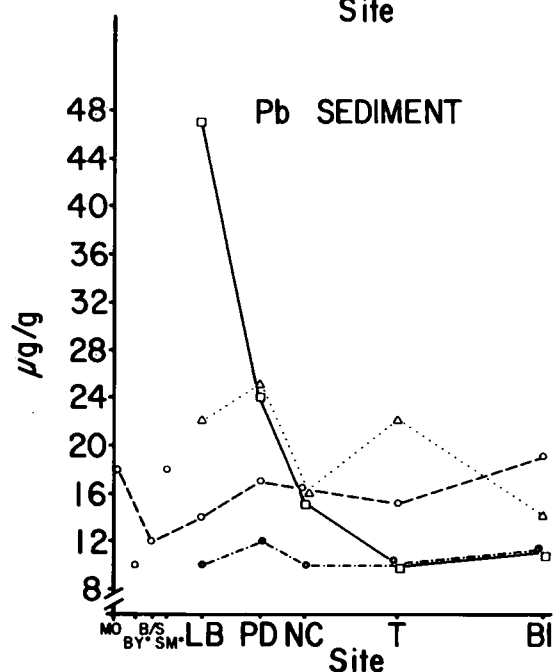
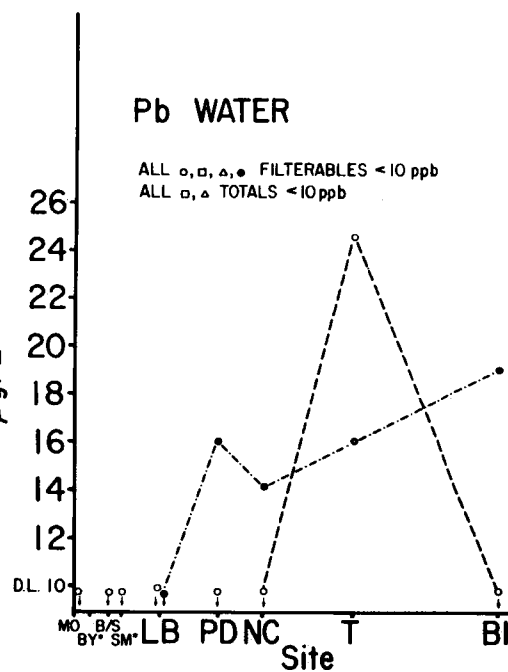


Figure 8e. Lead concentrations in water, suspended sediment and plant phases for the Bow and Oldman rivers. Distance between sites on graphs is proportional to actual river distances.

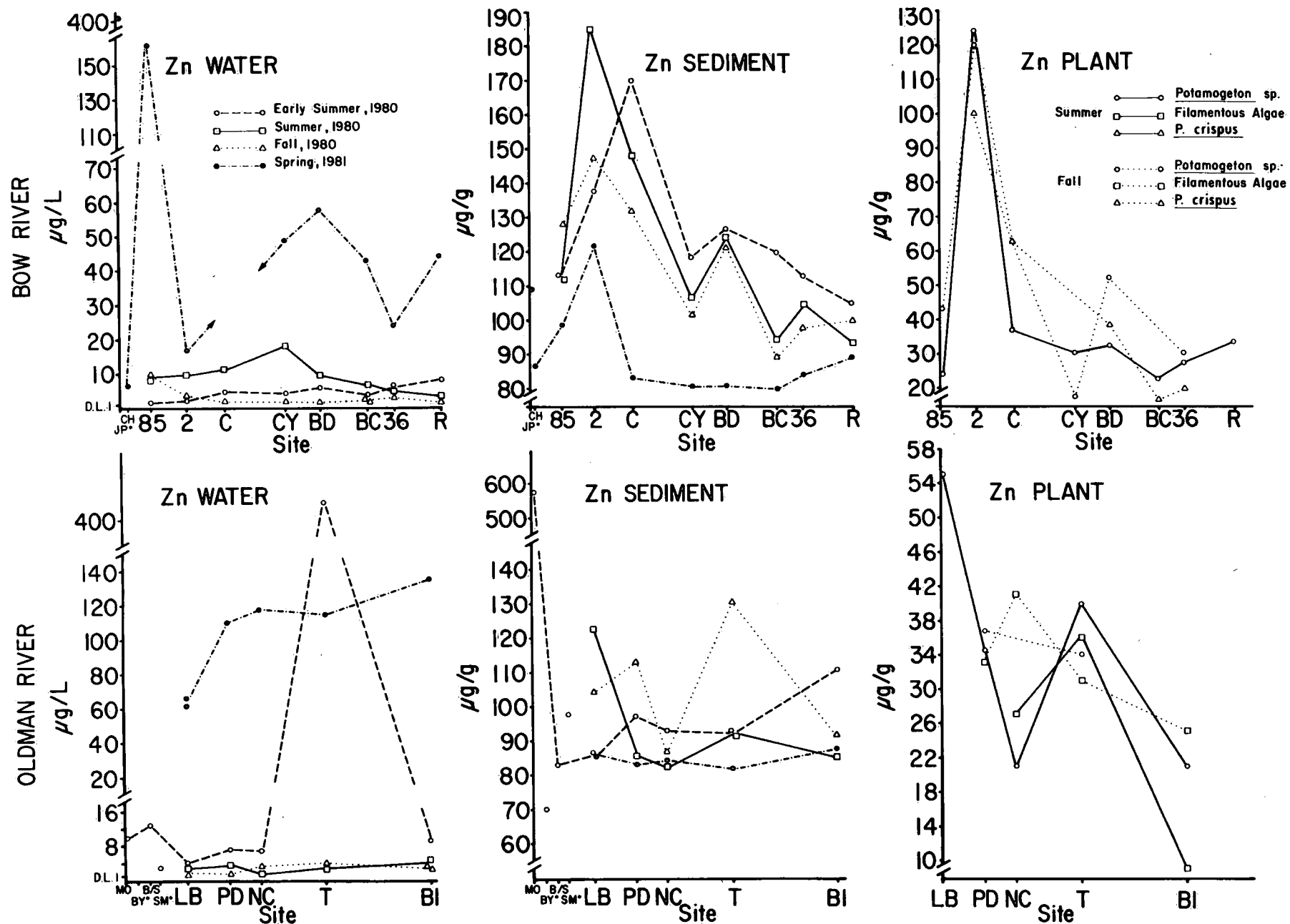
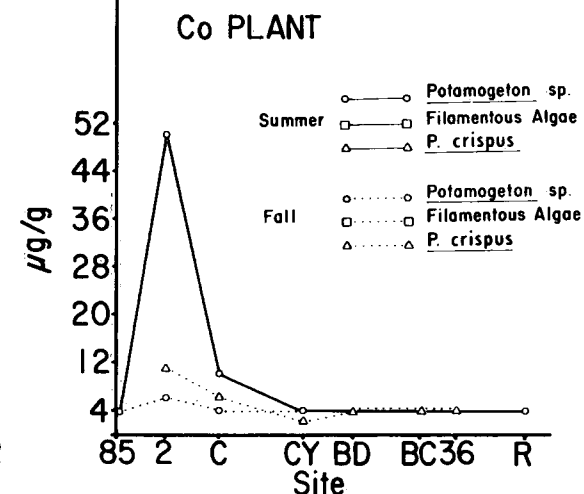
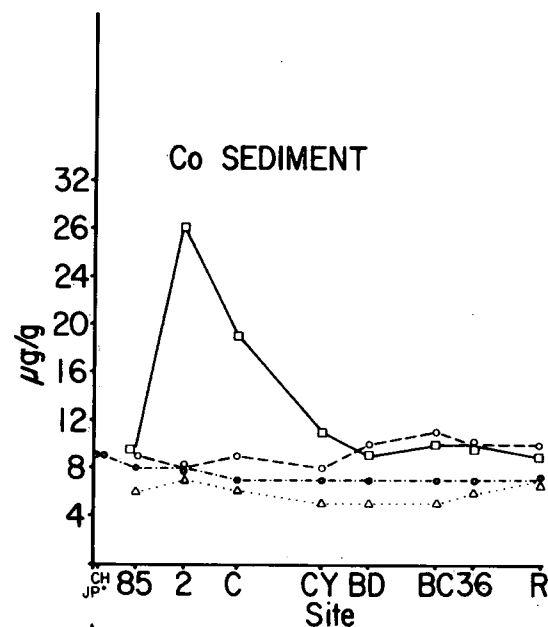


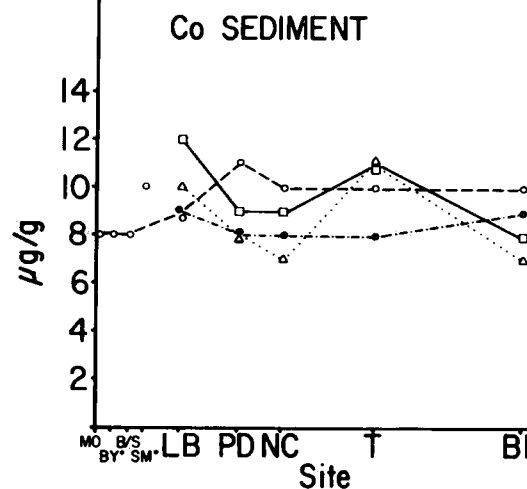
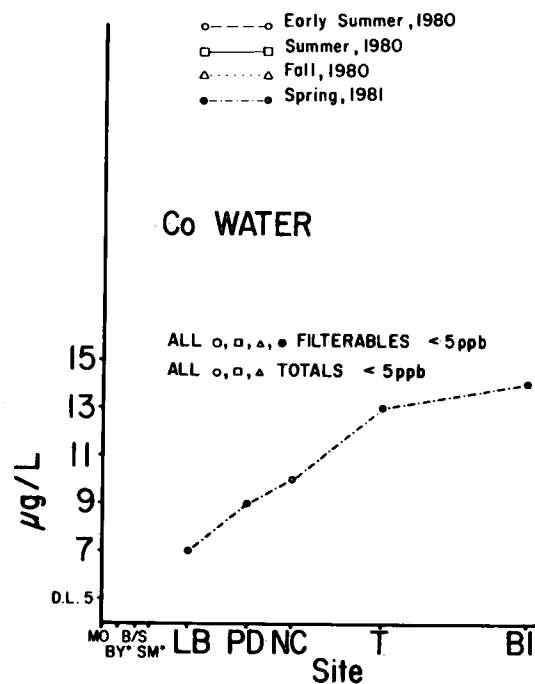
Figure 8f. Zinc concentrations in water, suspended sediment and plant phases for the Bow and Oldman rivers. Distance between sites on graphs is proportional to actual river distances.

# BOW RIVER

ALL TOTALS AND FILTERABLES  
< DETECTION LIMIT



# OLDMAN RIVER



ALL VALUES < DETECTION LIMIT

Figure 8g. 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.

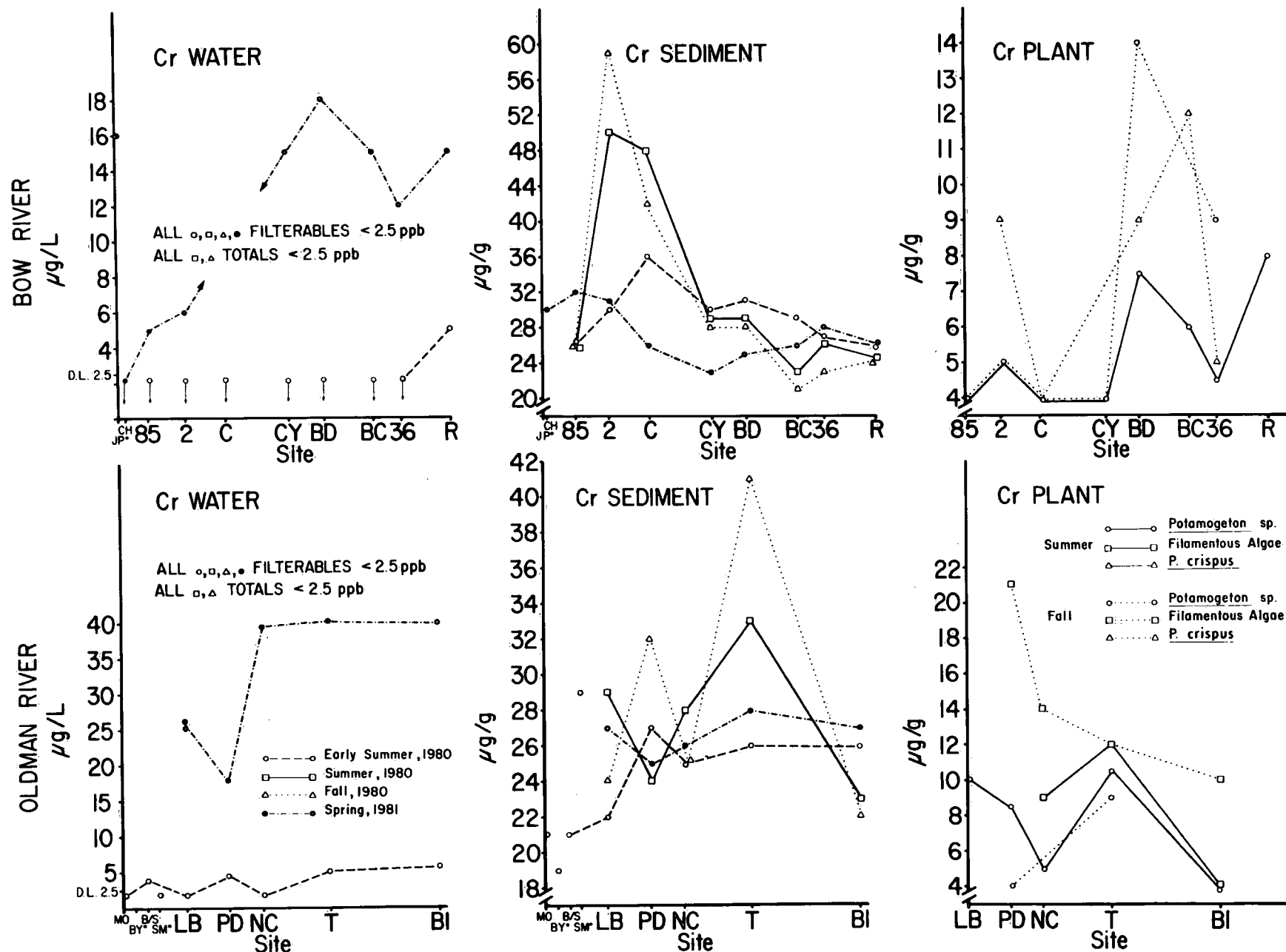
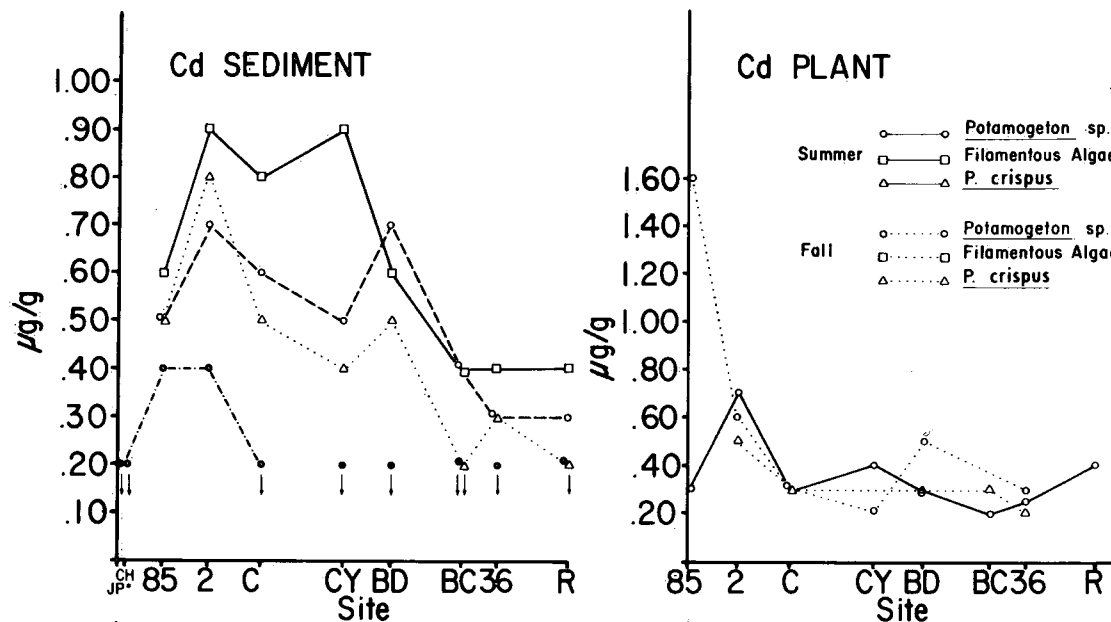


Figure 8h. Chromium concentrations in water, suspended sediment and plant phases for the Bow and Oldman rivers. Distance between sites on graphs is proportional to actual river distances.

# BOW RIVER



ALL TOTALS & FILTERABLES  
< DETECTION LIMIT

# OLDMAN RIVER

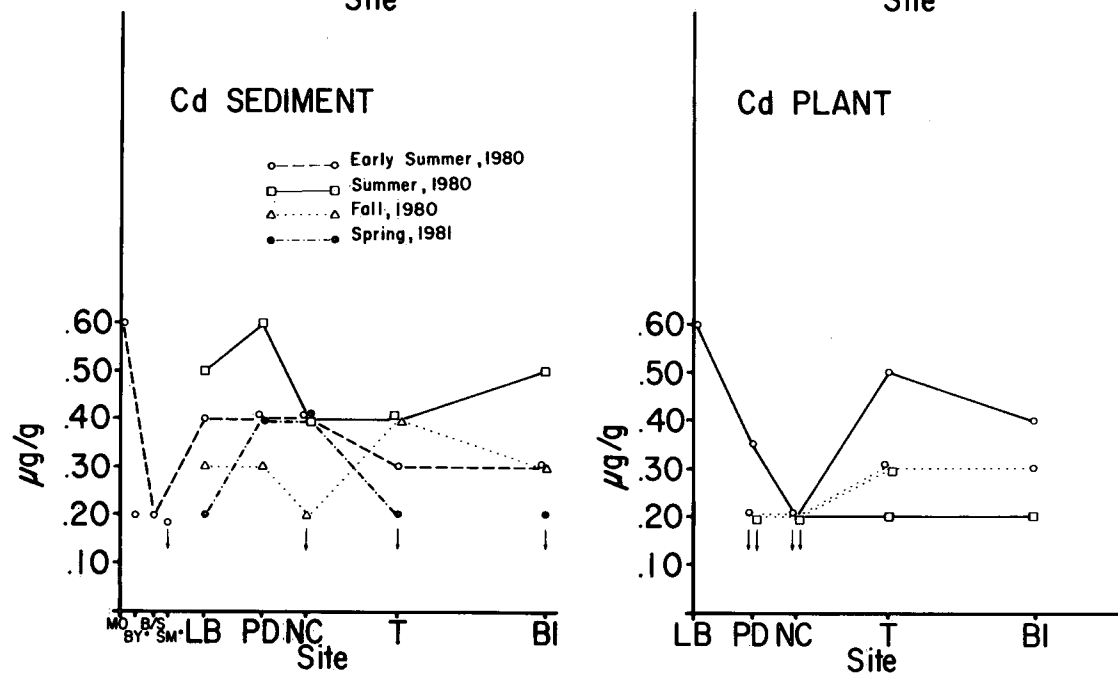


Figure 8i. Cadmium concentrations in water, suspended sediment and plant phases for the Bow and Oldman rivers. Distance between sites on graphs is proportional to actual river distances.

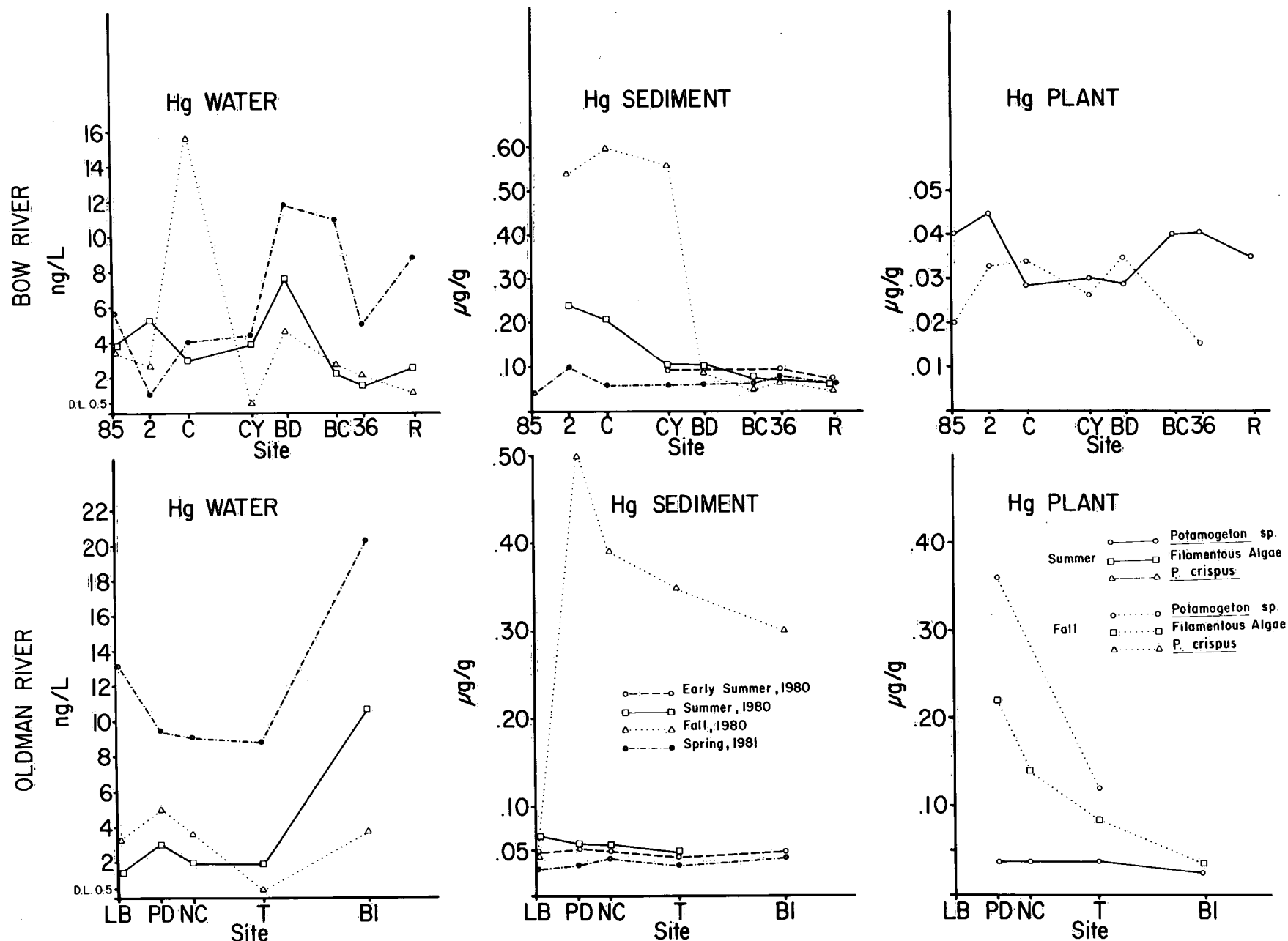


Figure 8j. Mercury concentrations in water, suspended sediment and plant phases for the Bow and Oldman rivers. Distances between sites on graphs is proportional to actual river distances.

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

"Total" values for most metals can be determined for other seasons. While still reflecting prairie runoff, early summer values are considerably lower than those 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 the "total" water sample. Concentrations for all metals in both rivers are the lowest in the fall, the period of least sediment transport.

Downstream trends in metal levels generally reflect suspended sediment concentrations and are particularly evident for total Mn, Fe, Cu and Zn in early summer in the Bow, and for Mn and Fe (in summer and fall) and Cu (fall) in the Oldman River.

#### *Suspended Sediment-associated Metals*

Seasonal changes in sediment-associated metal concentrations in the Bow and Oldman rivers indicate changes in suspended sediment concentrations, the impact of point sources, 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 and Hg are essentially at background levels in the spring. Diffuse source runoff, erosion and bank slumping contribute large quantities of solids to the river. These solids 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 and Hg found at BRBD and BRBC (1.95% and 396, 16, <0.2 and 0.016 mg/kg, respectively) compare closely with levels in bank material of 1.70% and 310, 07, <0.2 and 0.034 mg/kg (Table 4). Metal levels at background river sites (e.g. CH, BR85) have similar values. Spring sediment metal levels are in the same range as those on sediments from irrigation return flows (Joseph, 1982).

During periods of snowmelt, especially when coupled with regional rainfall, the concentration of sediment-related metals is largely determined by natural inputs of sediment with background levels of metal chemistry. In the early summer, summer and fall, metal concentrations on suspended matter appear to be directly influenced by inputs from Calgary and Lethbridge 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 presumably a direct response to inputs of metals from the Calgary area. The enriched sediments show a decline in concentration downstream, where sediment contributions of background metal content from the Elbow and Highwood rivers (entering the Bow between BR2 and BRC), from Arrowwood Creek (entering between BRC and BRCY), and from bank collapse, dilute the Bow River sediment chemistry. The increases in sediment concentration at BRC and BRCY (Fig. 2) 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 tenfold increase in sediment concentration. The reduced peak at BR2 reflects the greater sediment concentration during the spring runoff period; this serves to reduce the

Table 4. Metal Concentrations in Bank Materials

Metal (mg/kg)	Site					
	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	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Hg	0.061		0.040	0.027	0.040	

\*Duplicate analyses reported.

impact of contaminants from Calgary on a unit weight basis of suspended matter. Early summer trends in the Oldman River parallel those for spring data for Mn, Fe, Pb and Hg and show enrichment downstream from Lethbridge and the effect of tributary sediment inputs for Ni, Zn, Cr and Co.

The increase in concentration of many of the metals 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. The increase may also be accounted for by a slightly higher proportion of clay-size particles resuspended from the reservoir.

Summer concentrations of most of the metals are higher than those in spring and early summer. Although the organic content rises in the summer, sediment enrichment is more likely attributed to the lower concentration of suspended matter, and, therefore, a greater impact of the Calgary and Lethbridge point and urban diffuse sources per unit weight of sediment. Summer and fall peaks of several metals at the Taber site on the Oldman indicate an unidentified source in the Taber area. The elevated summer 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.

Fall concentrations are approximately equal to or lower than those of summer in the Bow and Oldman rivers with the exceptions of mercury and copper. Downstream trends are similar to early summer and summer trends, with peaks at BR2 and BRBD and subsequent declines in the Bow, and declines from ORPD in the Oldman. Differences exist in the Bow for Pb, Cu and Hg. Lead declines steadily from BR2 to BRR, suggesting that Pb is not being mobilized in measurable quantity from Bassano Dam sediments in the fall. The fall trend of Cu is very similar to the organic matter trend (with peaks at BR2 and BR36); Cu is known to be associated with organic matter. Concentrations of Hg decline sharply from BRCY to BRBD. The possibility of Hg being released from the sediments of the reservoir is supported by an increase in total-Hg in the water phase.

Sediment-Mn, Ni and Fe show unique relative seasonal concentrations and downstream trends. Manganese peaks in each season at BR85 decrease to a low level at BRC, then gradually increase downstream to background concentrations in the spring or higher than those levels in the fall. Iron is the highest in spring and early summer; trends in early summer and summer are similar (decreases at BR2, BRCY and 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.

#### *Aquatic Plant-related Metals*

Accumulation of most metals (Ni, Fe, Cr, Pb, Zn, Cu and Cd) is greater in Bow River plant samples collected in the fall than in the summer. Only Mn, Co and 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 undoubtedly 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 and Hg. For each of these metals, the concentration is approximately fivefold greater on suspended sediments (comparing all sites in summer and fall) in the Bow River.

Metal concentrations in Oldman River plants are higher in the fall than in the 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 approximately 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.

Summer and fall concentrations of Cu, Pb, Zn, Cr and Cd show concentration increases at BR2 and BRBD, with rapid declines downstream from these sites to at least background levels. Summer peak levels of Zn, Pb and Cd occur at BR2, while peaks of Cu and Cr occur at BRBD. In the fall, Zn reaches a maximum value at BR2, and Cu, Pb, Cr and Cd peak at BRBD. This suggests that over the growing season Zn is more available to macrophytes at BR2 (source of contaminants in solution) and that Cu and Cr are more readily available at BRBD (location of potential metal release from sediments).

Downstream trends in metal concentrations in the Oldman River are similar for *Potamogeton* sp. and



filamentous algae. The exception is Cr, for which the species trends differ in the fall. Significant summer peaks of Ni, Fe, Cu, Zn, Cr and Cd are found at ORT, suggesting that contaminant inputs from an unidentified source in the Taber reach are available. 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 (the plant was located midstream in a sheltered sedimentary location and was senescent). Fall trends show peaks at ORNC for Mn, Ni, Fe, Cu and Zn; the peaks are not mirrored in sediment-associated metals nor in water samples.

### Loading Scenarios

Loadings of heavy metals and phosphorus provide 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 and ORBI) on each river. Biomass load (for the Bow River) represents the cumulative load stored in 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 permits a comparison of loadings amongst the various phases (plant, sediment, water). Biomass load, because it is the cumulative load for the river, implies an amount that would be transported downstream into the South Saskatchewan River if all aquatic biomass were uprooted and transported downstream as organic mats without significant decay en route. This is an assumption that will vary greatly depending upon the hydrologic conditions that prevail in any particular year.

Loads in water (Table 5) 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–October) 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 mean 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 in metric tonnes.

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

Concentrations of some of the water- and sediment-related metals were below detection. In such cases metal concentration was assigned the detection limit and the load calculated accordingly. Loads of such metals are, therefore, maximized. 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 5) 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 biomass data were divided into reaches which correspond to the sampled sites. Biomass loadings assume 100% plant cover on the substrate of each reach; realistically, the cover should be reduced by 25% to 50% and the loadings reduced accordingly.

The importance of suspended sediment concentrations to water chemistry during high-water periods is 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 sediment concentrations rather than any substantial difference 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 (i.e. total) component and, we believe, reflect field sample contamination of that element.

For the entire six-month period the 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 [Joseph, 1982]), 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 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 the component associated with sediment is also determined. Unfortunately, the filtered component in spring and, for many metals, the total component during summer are usually less than conventional detection limits. This presents a problem for agencies not able to resort to more rigorous analytical procedures, especially

Table 5. Estimated Heavy Metal and Phosphorus Loads at the Mouth of the Bow and Oldman Rivers, May-October, 1980 (metric tonnes)

Site	Parameter	Total load in water			Load on suspended sediment			Storage in biomass*
		High water	Low water	Total	High water	Low water	Total	Total
Bow River at BRR	Pb	10.3†	5.2†	15.5†	4.8	0.2	5.1	42.6
	Zn	5.2	1.4	6.6	19.1	0.3	19.5	338.0
	Cu	7.6	0.8	8.5	5.7	0.1	5.8	30.8
	Ni	20.6†	2.6†	23.2†	4.9	0.1	5.0	46.9
	Cr	9.9	1.3†	11.2†	4.6	0.1	4.7	23.5
	Cd	1.0†	0.5†	1.5†	0.1†	0.0†	0.1	2.1
	Co	5.1†	2.6†	7.7†	1.6	0.6	2.2	69.5
	Mn	107.4	4.6	112.1	104.5	3.7	108.2	1 522.0
	Fe	5 584.9	156.4	5 741.3	4 305.1	78.3	4 383.5	872.0
	Hg	$8.9 \times 10^{-3}$	$9.7 \times 10^{-4}$	$9.9 \times 10^{-3}$	$1.2 \times 10^{-2}$	$1.6 \times 10^{-4}$	$1.3 \times 10^{-2}$	0.1
	P	247.9	32.4	280.4	223.1	52.6	275.8	13 581.0
Oldman River at ORBI	Pb	15.9†	2.6†	21.2†	10.6	0.0	10.6	
	Zn	81.9	0.6	82.6	70.7	0.1	70.9	
	Cu	22.1	0.2	22.4	21.6	1.4	23.1	
	Ni	26.2	1.3†	27.5†	18.4	0.0	18.5	
	Cr	26.4	0.6†	27.1†	18.8	0.0	18.8	
	Cd	1.1†	0.2†	1.4†	0.3	0.0	0.3	
	Co	11.6†	1.3†	12.9†	6.7	0.0	6.7	
	Mn	429.2	2.4	431.6†	364.2	28.2	392.5	
	Fe	20 623.0	98.4	20 820.0	16 078.0	478.5	16 556.0	
	Hg	$2.3 \times 10^{-2}$	$1.9 \times 10^{-3}$	$2.5 \times 10^{-2}$	$3.3 \times 10^{-2}$	$5.8 \times 10^{-1}$	$6.2 \times 10^{-1}$	
	P	345.7	6.8†	352.6†	622.4	10.8	633.2	

\* 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.

when dealing with large rivers where net flux or low-level metals can be significant.

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 bioavailable 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 nutrients which will be transported downstream during periods of high discharge 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. the 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 nutrients and metals are released back into the water column during decay once the organic material is in transit or has been deposited. The 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.

For comparison with data of Table 5, Alberta Environment (Hamilton, personal communication) has calculated annual anthropogenic (sewage, industrial and urban runoff sources) loadings to the Bow River in 1980 for Cr (5.3 tonnes), Cu (3.5 tonnes), Pb (9.8 tonnes) and Zn (21.3 tonnes). That there should be differences between Table 5 and these anthropogenic loads is not surprising, bearing in mind the different nature of the calculations and the fact that the data of Table 5 were obtained at the mouth of the Bow. Nevertheless, a comparison of these data is instructive. Anthropogenic loads of three metals (Cr, Cu, Pb) are much less than the six-month values in Table 5, whereas Zn greatly exceeds our calculation. As noted above, our data demonstrate the significant extent to which annual load is dominated by large quantities of unenriched suspended sediment carried during a short period of the year. The anthropogenic contribution to measured flux of Cr, Cu and Pb (or any other metal) is likely to be relatively small. Also, and as is seen in the higher anthropogenic values of zinc, a very significant proportion of the anthropogenic load is likely removed by biomass. Our data show a large uptake of zinc in plant material immediately below Calgary (Fig. 8f). Therefore, it is entirely likely that the bulk of the anthropogenic load is lost to biomass long before it reaches BRR (where our load calculations were made). This, obviously, has

certain practical implications for measurement programs at the mouth of the Bow which exclude considerations of biomass.

### Organochlorine Residues

An aspect of the project was to establish pathways and characteristic distributions of a suite of nonionic pesticides, PCBs and chlorobenzenes in the water, suspended sediment and plant phases (Ongley and Blachford, 1982a,b). Pesticides and PCB residues characteristically have low solubility and 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). The pesticide DDT, dieldrin and PCBs 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 compounds. 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 was limited by the low to nil presence of many of the organic residues. A number of the pesticides (e.g. 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. The samples were screened in duplicate for all common organochlorine pesticide residues, including  $\alpha$ -HCH,  $\beta$ -HCH and  $\gamma$ -HCH;  $\alpha$ -chlordane,  $\gamma$ -chlordane and oxy-chlordane; aldrin; endrin; dieldrin; heptachlor; HE; methoxychlor; DDT and its metabolites; mirex; photomirex; and PCBs. However, only the residues found in at least one of the sediment, plant or water phases are reported here. Because most of the detectable residues are at, or close to minimum detectable levels, the results (Fig. 9) 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 adsorption constants of the residues, the association with and potential for uptake by aquatic vegetation, and the hydrologic characteristics of the sampled fluvial regimes.

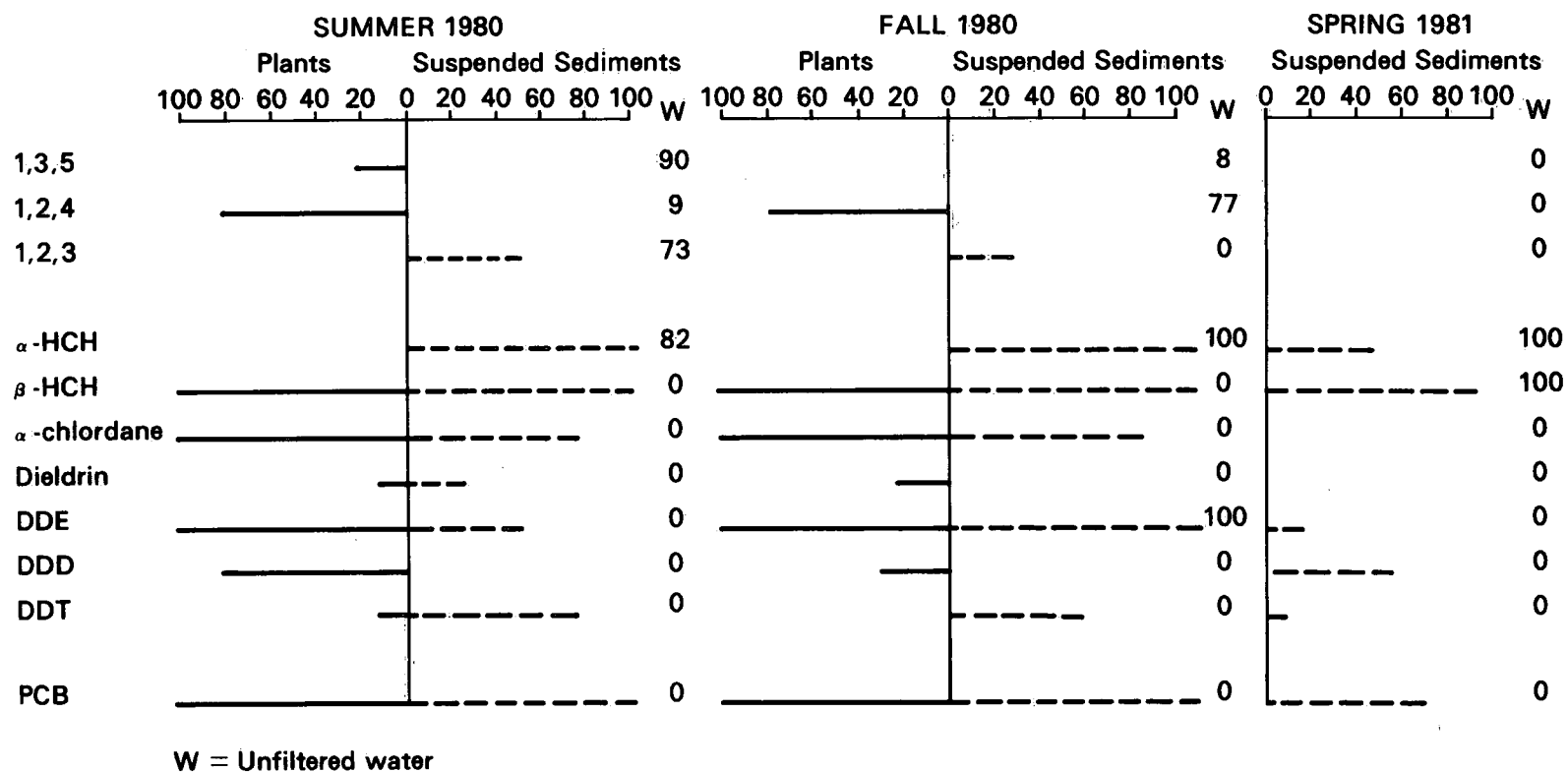


Figure 9. Seasonal phase distributions of chlorobenzenes, organochlorines and PCBs for the Bow and Oldman rivers. The values for plants, suspended sediments and water (W) samples indicate the percentage of samples in which detectable quantities of the substances were found. Plant matter was not sufficiently available in the spring.

Solubility of the organochlorine residues ranges from 0.001 ppm (Weber, 1972) for DDT to 637 ppm (Hague *et al.*, 1977) for one of the PCB isomers. Increasing chlorination decreases solubility of the compounds. Except for  $\gamma$ -HCH (which was not present in our samples) the chlorinated hydrocarbon insecticides and PCBs are considered insoluble in water (Weber, 1972). This is evident in their absence in the water phase in each season. In the fall DDE is present in water, possibly 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 with 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).

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. As  $\beta$ -HCH,  $\gamma$ -chlordane and DDE indicate equal or greater accumulation in the plant than in the sediment phase, 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 suspended sediment; DDD is found only in plant material. However, the absence of DDD in sediment may be due to dilution of sediment-DDD by additions of DDD-free sediment 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-chlorobenzene 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 ( $K_d$ ) 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  $K_d$  values are essentially those that are expressed in Figure 9, with the inclusion of the plant phase.

## SUMMARY AND MANAGEMENT IMPLICATIONS

Over the six-month period (May–October) 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 during high spring flow indicates that suspended sediment chemistry is at background levels and is not of biological relevance in that season.

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 metals are due, at least in part, to dilution of enriched suspended matter by bank collapse and tributary inputs of unenriched sediments. Interpretations of downstream reductions of nutrient and contaminants must, therefore, be treated with caution unless, as in this study, direct measurements of contaminants and of phosphorus species are made on sediments and biomass.

### Phosphorus

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. 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.

Total and filterable phosphorus are useful measures in characterizing spatial and temporal changes in phosphorus flux. For management purposes both variables are required to characterize the conversion of TDP (as a surrogate for bioavailable P) to particulate form, the loss of phosphorus load as TP concentrations change in a downstream direction, and the total phosphorus flux, given that the particulate fraction does contain phosphorus which can become bioavailable under certain sink conditions. The chemical measures do not account for the large loads of phosphorus that are associated with biomass.

The particulate load comprises unavailable apatite-P, and potentially available NAI-P and O-P. While these latter two forms may not be important in the fluvial 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, while the NAI-P and O-P fractions predominate in other seasons.

For downstream management purposes, sediment-associated phosphorus forms should be characterized on a seasonal basis within each watershed. Since there is little variability between sites during high flows in spring, 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 neither cost-efficient nor scientifically defensible to determine speciation variance in view of the many other forms of variance introduced in the process of calculating a sediment-associated phosphorus load over an extended period (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 bioavailable P, TP-TDP does measure the change from solute to unavailable (in rivers) phosphorus. This is important, as the data indicate that there is a large and potentially available (in a reservoir context) sediment-associated phosphorus load in low flow months when suspended sediment concentrations are very low.

For management purposes aquatic plants present advantages and disadvantages. They extract phosphorus (and other elements) from the water column, thereby effecting in-stream tertiary treatment. However, the accumulated phosphorus loads 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 a sink environment.

For monitoring purposes, phosphorus concentration in macrophytes appears not to be a useful indicator of nutrient stress. Total-P in plants reflects not only bioassimilated-P but also phosphorus associated with entrapped mineral material and precipitates. Changes in TDP are not directly reflected by plant-P, as plants concentrate phosphorus to a greater extent in nutrient-poor waters. 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, disregard the impact of short-term releases of nutrient-rich effluent which may make other control programs ineffective.

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 with a significant macrophyte or sessile algal population requires the measurement of plant-associated phosphorus. The 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.

### Heavy Metals

Most filterable and many "total" measurements of metals in water are below conventional detection limits. In spring, metal levels tend to be approximately tenfold 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.

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 is a serious and limiting attribute of conventional chemical measures. For metals 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.

Metals on suspended sediments 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 similar to the 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. 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 desorption occurs between BR2 and BRCY, where many sediment-metals have returned to values close to those immediately upstream from Calgary (BR85). Reductions are likely caused by additions of suspended sediment having low background chemistry 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 the 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.

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 downstream trends similar to sediment-associated metals, especially for Ni, Zn, Cd and Pb in macrophytes of the Bow River. Elevated levels of metals in plants usually occur over short distances

below a point source; they are not attenuated in the downstream direction as in the case of suspended sediment. 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 peak below Lethbridge and again 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. Plants not only integrate metal uptake through time but also are a measure of metal bioavailability. 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 that are not detectable in water are easily found in aquatic plants. Plant data indicate that bioavailable metals are diminished to nearly background levels by Carseland on the Bow River; this observation is not possible with water or suspended sediment chemistry.

Significant plant uptake implies a major loading which is temporarily stored in biomass. With the exception of iron, loadings of metals in biomass greatly exceed measured chemical flux. 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. The degree to which this could be a problem in the South Saskatchewan system is not known. Significant storage of metal (and phosphorus) loads in biomass, however, does imply that metal (and phosphorus) loads calculated from conventional data are greatly in error regardless of the frequency of chemical measurements.

### Organochlorine Residues

Of the suite of organochlorine residues scanned, only the following residues were detected: 1,3,5-chlorobenzene, 1,2,4-chlorobenzene and 1,2,3-chlorobenzene;  $\alpha$ -HCH and  $\beta$ -HCH;  $\alpha$ -chlordane; dieldrin; DDE/DDD/DDT; and PCBs. These were found at or near detection limits. Significantly, only the chlorobenzenes and  $\alpha$ -HCH were routinely detectable in "total" water samples. The remaining detectable substances are associated primarily with suspended matter and/or plant material. Results indicate that many organochlorine residues preferentially associate with one or more of the sediment/plant/water phases.

The management implications of the organochlorine residue levels lie 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 use of aquatic plants for detection of modern, more soluble and degradable biocides has 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 problem 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.

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