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Temporal Variability of Phosphorus Levels in the Flathead River at the International Border

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ABSTRACT

A three year study of water quality in the boundary reach of the Flathead River was undertaken to determine the temporal variability of total phosphorus (TP) and total dissolved phosphorus (TDP) levels. This investigation, designed to provide information for the development of a compliance monitoring program, involved intensive sampling of TP and TDP over the spring freshet period and intermittently over the low flow period. In addition, three 24 hour studies were undertaken to assess short-term variability. TP and TDP concentrations ranged from <0.002 to 0.48 mg/l and from <0.002 to 0.035 mg/l, respectively, with the highest levels recorded at the peak of freshet. Over the low flow period the concentrations of both variables were consistently near the detection limit (0.002 mg/l). Fluctuations in the levels of both TP and TDP were positively correlated with changes in streamflow, and reflect increases in suspended sediment concentrations. These results indicate that monitoring programs designed to assess compliance with water quality objectives must take into account the natural variability of phosphorus levels.

INTRODUCTION

The waters of the Flathead River system generally contain very low levels of the major plant growth nutrients, nitrogen and phosphorus. Studies undertaken in the basin over the past ten years have indicated that most of the lotic and lentic waters in the basin are phosphorus limited (Sheehan et al. 1980; Zacheim and Cooper 1983). However, it is apparent that nitrogen levels may also limit productivity during certain portions of the year, particularly in the late summer in some waters (Stanford et al. 1983; D. Valiela pers. comm.). Consequently, land-use developments that have the potential to increase levels of these plant nutrients are of particular concern because very small increases of phosphorus and/or nitrogen could stimulate abnormal growth of algae in affected streams.

Formulation and implementation of site-specific water quality objectives for phosphorus designed to control algal growth would facilitate water management in this system. Due to the importance of reliably detecting small changes in nutrient concentrations this paper examines temporal variability of phosphorus levels. Conclusions derived from this work can be used to design phosphorus monitoring programs for compliance with objectives or detection of long-term trends.

STUDY AREA

The Flathead River, after flowing almost 70 km from its headwaters in the Rocky Mountains, crosses the international boundary on its way to Flathead Lake in the State of Montana, and ultimately joins the Columbia River system (Figure 1). In the Canadian portion of the basin, the Flathead River system drains an area of approximately 1,582 square kilometers. The long-term mean annual discharge (1952 -1986) recorded at the border station is 26.6 m^3/sec (940 ft^3/sec) (Environment Canada 1987b). The Flathead is typical of continental interior type drainage basins with a snowmelt driven hydrograph, with over 70 percent of the annual discharge occurring during spring freshet (April - June).

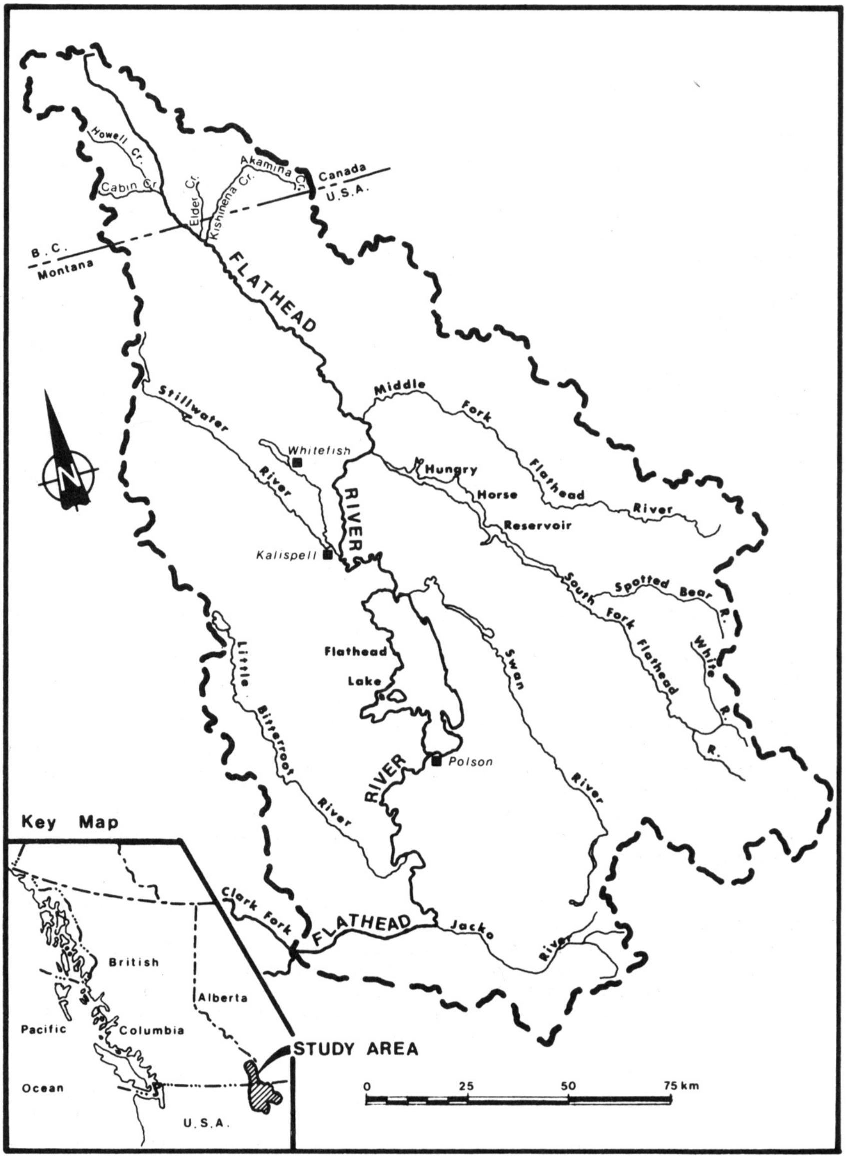

Figure 1. Map of the Flathead River Basin.

BACKGROUND

The Canadian portion of the drainage basin, until recently, has remained relatively pristine. In the past, developmental activities in the basin had been limited to some small-scale timber harvest and mineral exploration. In recent years infestations of forest insects have induced large-scale cutting operations to salvage affected timber. In addition, coal and oil deposit discoveries have increased activity in the area. Oil and gas developments have been proposed, and may include the construction of a carbon dioxide purification facility and pipeline to transport the extracted carbon dioxide gas. Coal deposits in the Howell Creek area (10 km north of the international boundary) are considered extensive enough to sustain intensive mining activities for more than 20 years. All of these existing and proposed developments have the potential to increase the levels of phosphorus in the Flathead River.

In the United States, the North Fork Flathead has been designated a recreational and scenic river under the Wild and Scenic Rivers Act. Introductions of phosphorus into the system have the potential to stimulate abnormal growth of algae, and thereby impair recreational and aesthetic uses of water on both sides of the border. The development, negotiation, and implementation of water quality objectives (WQOs) form a basis for co-operative water quality management in this basin. However, for water quality objectives to be effective, cost-effective compliance monitoring programs must be designed and implemented. Optimization of these monitoring programs requires information on the natural variability of water quality variables in order to maximize the probability of detecting exceedances.

METHODS

(a) Field Sampling

As part of an integrated study of water quality in the Canadian portion of the Flathead River basin, a sampling station was established on the Flathead River at the international boundary. This site, known as the Flathead River at Flathead (00BC08NP001), is located at the Water Resources Branch (Environment Canada) gauging station approximately 100 m upstream of the international boundary.

Water quality sampling was conducted over the period November, 1983 to February, 1987. Over this period, a total of 544 and 374 samples were collected for analysis of total and total dissolved phosphorus, respectively. Approximately 75 percent of the sampling effort was expended during the period of spring freshet (April - June) at this site to ensure representative sampling over a range of stream flows.

Water quality sampling was conducted over three distinct time scales to assess temporal variability of phosphorus levels in this system. Three twenty-four hour studies were conducted during low (approx. 4 m^3/s), moderate (approx. 50 m^3/s), and high (approx. 160 m^3/s) flow periods to assess short-term variability. These short-term studies included simultaneous sampling at three points along the cross section. Seasonal variability was studied by conducting sampling during selected periods throughout the year, with emphasis on the freshet period. Year to year variability was addressed by conducting the study over a three year period.

Six replicate samples for TP analysis were taken simultaneously in 50 ml glass bottles at each sampling time to assess instantaneous within-sample variability (after Kleiber and Erlebach 1977). Similarly, replicate TDP samples were collected simultaneously in 100 ml glass bottles. Initially six, and subsequently three replicates were collected when it was established that there was little variability between replicates for filtered P samples. Total dissolved phosphorus samples were filtered in the field through 0.45 µm millipore filters into 50 ml glass bottles. In addition, six blanks and six filtered blanks were prepared in the field for analysis of TP and TDP: analysis of these samples indicate no background contamination. The samples were subsequently transported to the laboratory in coolers and stored at 4°C until analyzed. Laboratory time series analyses indicated that the levels of phosphorus measured in individual samples collected during high and low flow periods were not dependent on storage time.

(b) Laboratory Analyses

The methods used to perform the chemical determinations of TP and TDP are based on colourimetry on an autoanalyzer, and are described by Naquadat Method numbers 15406 and 15102 in the Analytical Methods Manual (Inland Waters Directorate 1974). All of the phosphorus analyses were performed by the Analytical Services Division of the Water Quality Branch (Pacific and Yukon Region). The accuracy of these methods is considered to be better than +/- ten percent.

(c) Data Analyses

Levels of particulate phosphorus (PP) in water were calculated by subtracting the mean total dissolved phosphorus (TDP) concentration from the mean total phosphorus (TP) concentration. Water chemistry data were input into a mainframe computer using Oracle data base management software. The data were subsequently downloaded to an IBM PC compatible microcomputer and converted to Lotus 123 format. Statistical analyses were completed within the Lotus environment.

RESULTS

(a) Instantaneous Variability

The instantaneous variability of phosphorus levels in the Flathead River was assessed by replicate sampling. Even in the cases where the coefficients of variation were the highest, a relatively stable estimate of the mean was obtained after the third replicate (see Figures 2 and 3). On a practical basis, therefore, three or more replicate samples appear satisfactory for sampling total phosphorus and total dissolved phosphorus in the Flathead River. There was no systematic difference in coefficient of variation between total phosphorus and total dissolved phosphorus (see Table 1), but for both variables the coefficient of variation was lowest at freshet. It should be emphasized that this conclusion refers to variability among replicates taken at the same time (and therefore the same flow conditions) and does not refer to flow-related variability, which is expected to be high at freshet and is discussed below. Figures 4 and 5 show the instantaneous variability of TDP and TP concentrations, as the 95 percent confidence intervals around each mean and the minimum and maximum values observed for each sampling time, over the study period.

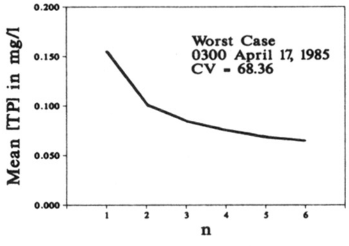

Figure 2. Estimated mean values of TP as a function of number replicates.

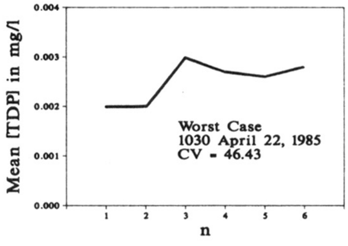

Figure 3. Estimated mean values of TDP as a function of number of replicates.

Table 1. Coefficients of variation of TP and TDP replicate samples in the Flathead River.

Date	Coefficient of Variation(%)[1]	
	TP	TDP
February 19-20/86	23.31	19.13
April 16-17/85	13.44	22.98
June 8/85	12.45	12.45

[1] Represents the mean within replicates coefficient of variation.

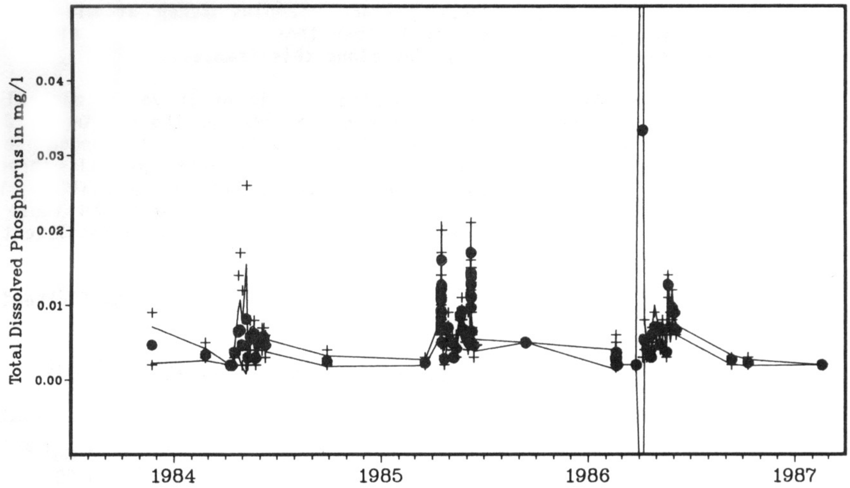

Figure 4. Instantaneous variability of replicate samples of TDP levels in the Flathead River (showing means as circles, maxima and minima as crosses, and 95 percent confidence intervals connected by a line).

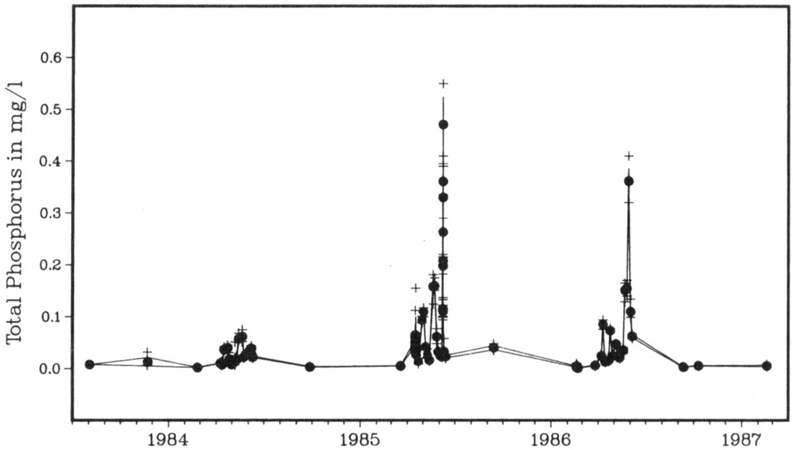

Figure 5. Instantaneous variability of replicate samples of TP levels in the Flathead River (means, maxima, minima, and 95 percent confidence intervals represented as in Figure 4).

(b) Short-term Variability

The short-term variability of phosphorus levels in the international reach of the Flathead River was assessed by measuring diurnal fluctuations during periods of low (February 19 - 20, 1986), moderate (April 16 - 17, 1985), and high (June 8, 1985) flow in the system. The results of these studies are summarized in Table 2. Analysis of variance of these data indicated that, at low flow, concentrations of TDP and TP did not vary significantly over the twenty-four hour period. During that interval, streamflow remained relatively constant and suspended sediment levels were very low (< 5 mg/l). There were no statistically significant differences in levels of TP or TDP from samples taken at three points along a transect at low flow.

During the period of moderate flow, the stage height varied only slightly. Concentrations of TP and TDP were variable, but did not differ statistically significantly from sampling time to sampling time during the twenty-four hour period. Samples taken at mid-stream had significantly higher levels of TP than those taken near the right or left banks. TDP levels did not differ along this transect.

During the high flow period, levels of TP varied markedly over time. The highest concentrations were recorded on the morning of June 8, corresponding to the peak of streamflow and of suspended sediment concentrations. This relationship is also evident when all three flow conditions are compared. There was a marked elevation in TP concentrations in samples taken at mid-stream compared to those taken near either bank. Along the transect, levels of TDP were consistent.

Table 2. Short-term variability of TDP, PP, and TP in the Flathead River at the international border.

Date	Time	Discharge[1]	[TDP][2]	[PP][2]	[TP][2]
Feb. 19/86	0730	-	0.002	0.002	0.004
	1230	3.95	0.003	0.001	0.004
	1730	-	0.002	0.002	0.004
Feb. 20/86	0900	4.16	0.002	0.000	0.002
Apr. 16/85	0930	-	0.008	0.036	0.044
	1230	51.3	0.010	0.034	0.044
	1530	-	0.009	0.039	0.048
	1830	51.1	0.010	0.030	0.040
Apr. 17/85	0300	51.7	0.014	0.034	0.048
Jun. 08/85	0930	164	0.015	0.372	0.387
	1530	162	0.013	0.210	0.223
	2130	148	0.011	0.102	0.113

1 Discharge (in m^3/s) estimated from gauge height readings.
2 Phosphorus levels (in mg/l) are averages for cross-section (n=9), and PP was calculated by TP - TDP.

Diurnal variability is therefore of concern for sampling TP and TDP in the Flathead River at the boundary during the high streamflow period. Variability in TP concentrations along transects is also a factor to consider, especially during high and moderate flow periods.

(c) Seasonal Variability

Levels of phosphorus in the international reach of the Flathead River varied significantly on a seasonal basis, as shown in Figures 4 and 5. Concentrations of TDP were lowest (< 0.002 mg/l) during periods of low flow. Levels increased with increasing streamflow, and generally peaked (to 0.035 mg/l) during the peak of spring freshet. TP concentrations followed roughly the same pattern; however the magnitude of the concentration change was larger (< 0.002 mg/l at low flow to 0.480

mg/L at the peak of freshet). At low flow, TDP constitutes half of TP, while at peak flow TDP is only one-twentieth of TP. While the concentration of TP at peak flow increased by about a factor of sixty from that at base flow, the concentration of TDP peaked at about six times its low flow concentration.

Figures 6 through 8 show the relationships between each of the forms of phosphorus and total suspended sediments (Environment Canada 1986a, 1987a, 1988). The regression coefficient is much greater for particulate phosphorus than for dissolved phosphorus, indicating the greater dependency of the former on flow and suspended sediment concentrations which in turn depend on flow. Again, however, it should be noted that there is a significant positive correlation between TDP and total suspended sediments (see Figure 7).

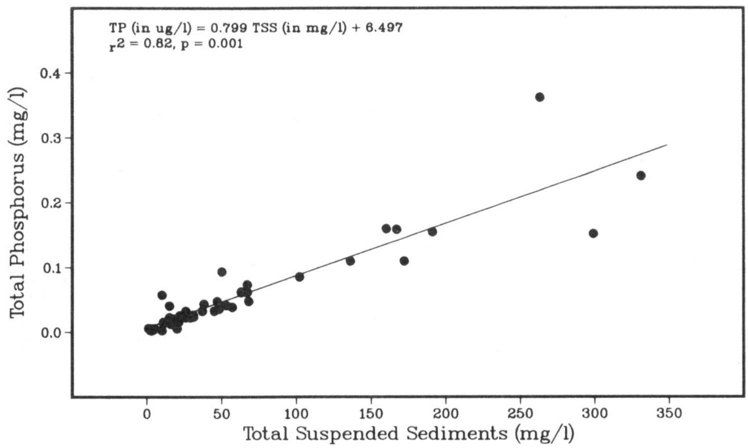

Figure 6. Relationship between TP and suspended sediment in the Flathead River.

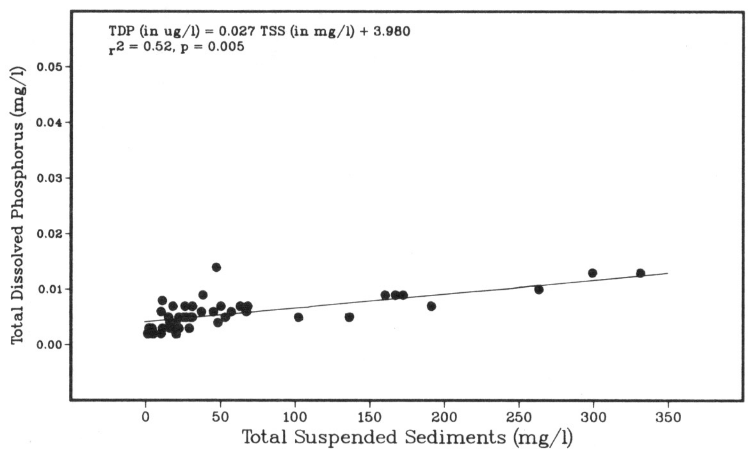

Figure 7. Relationship between TDP and suspended sediment in the Flathead River.

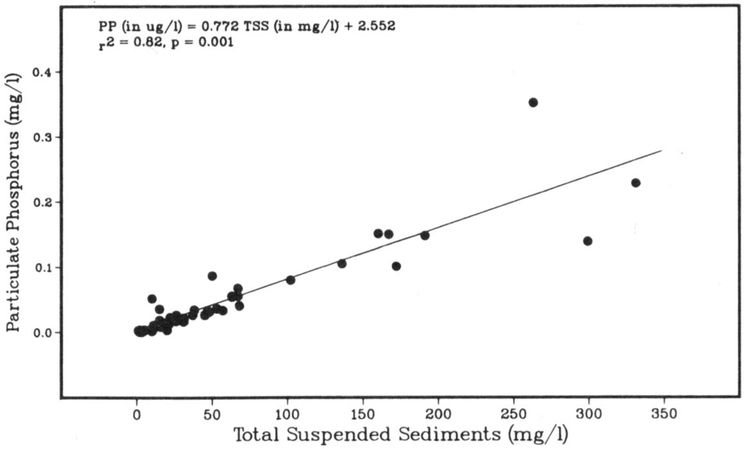

Figure 8. Relationship between PP and suspended sediment in the Flathead River.

The change in concentrations of TP and TDP with time can be much greater at freshet than during the rest of the year (see Figures 4 and 5), corresponding to the changes in flow rate. To take account of this variability, seasonal data were gathered so as to increase in frequency as flow rate increased. The results showed a pronounced hysteresis, so that a general predictive relationship between river discharge and phosphorus would require separate consideration of ascending and descending limbs of the hydrograph.

(d) Annual Variability

Concentrations of phosphorus in the Flathead River at the international border during low flow periods were not significantly different between years. However during spring freshet marked differences were evident and appeared to be related to differences in peak streamflows and suspended sediment concentrations between years (Figure 9). Concentrations of TDP were greatest in the spring of 1986, whereas concentrations of TP were greatest in the spring of 1985 (Figure 4 and 5). Both TP and TDP were relatively low in 1984, a year of low runoff. The peak concentration of TP in 1984 was only one-tenth of that in 1985. Peak runoff and peak phosphorus levels occurred in late May or early June in all three years studied.

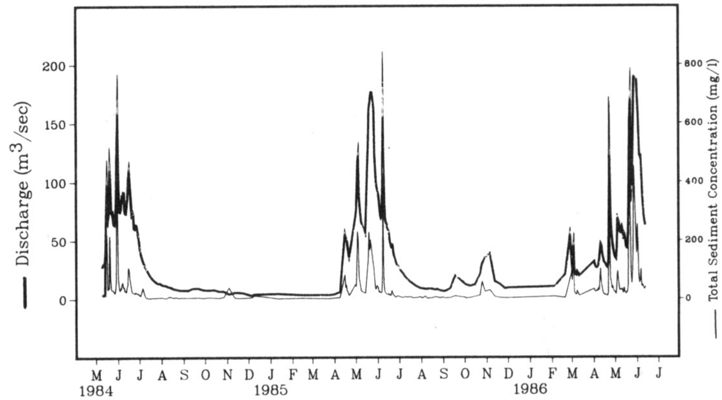

Figure 9. Daily discharges and suspended sediment concentrations in the Flathead River over the study period (Environment Canada 1985, 1986a, 1986b, 1987a, 1987b, 1988).

DISCUSSION AND CONCLUSIONS

The results of the replicate sampling and sampling at three points along a transect showed that, at least in surface water sampling in this river, triplicate samples for TP or TDP are probably appropriate. Replication is more important at low flow than at freshet, where the within-replicates coefficient of variation is lower than at low flow. The concentration of TP, but not of TDP, can be expected to differ along a transect from bank to bank at many times, but especially at high discharge.

The results of the present study indicated that phosphorus levels in the international reach of the Flathead River vary significantly on daily, seasonal, and yearly bases, with the bulk of the variability related to changes in streamflow and suspended sediment concentration. Fluctuations in the particulate (TP - TDP), dissolved (TDP), and total (TP) forms of phosphorus corresponded to changes in discharge. All three forms of phosphorus exhibited marked hysteresis effects when plotted against discharge. These results indicate that phosphorus levels are highest during the rising limb of the hydrograph, and that levels drop more rapidly as streamflows decrease. Similarly, variations in streamflow resulted in changes in suspended sediment concentration, as illustrated in Figure 9. Levels of suspended sediment reflect changes in the supply of sediment to the stream system. During rain events or periods of snowmelt, sediment supply increases due to increases in mass soil movements, and in the rates of surficial and fluvial erosion. Surficial erosion and mass soil movements result in the transport of sediment from terrestrial sites. Fluvial erosion is associated with high streamflows, and results in the transport of sediment stored on streambanks, in stream-beds, and in ephemeral stream channels. As streamflow decreases, recently active sediment sources become less important, and suspended sediment levels drop rapidly.

It is apparent that both phosphorus and suspended sediment levels vary in relation to discharge in the Flathead River, and that phosphorus levels reflect changes in suspended sediment concentration. The relationships between phosphorus levels and the concentrations of suspended sediment in this stream reach were determined by least squares regression (presented Figures 6, 7, and 8). This analysis indicated significant correlations between total and particulate P and suspended sediment concentration. TDP varied much less than particulate P, but was still significantly positively correlated with discharge and suspended sediment concentration. It is, therefore, evident that much of the phosphorus transported by the Flathead River is associated with suspended sediments. Stanford et al.(1983) obtained similar results at a station located downstream of the border (at Holt), where a significant, positive correlation between suspended sediment concentration and TP was observed. This relationship between discharge/suspended sediment concentration and particulate P has also been well documented in other freshwater systems (Prairie and Kalff 1988a; Munn and Prepas 1986; Rigler 1979; Meyer and Likens 1979). Laboratory studies of algal growth relative to levels of particulate phosphorus suggest that about ten percent of the phosphorus bound to sediments in the Flathead River is bio-available (Ellis and Stanford 1988). Thus the Flathead River carries a substantial load of biologically inert phosphorus during the spring run-off, and relatively high levels of dissolved phosphorus. Thus the expected increment in bioavailable phosphorus at freshet would include about ten percent of the particulate P plus most of the elevated levels of TDP (about 6X increase over low flow conditions). Whether or not this increased potential for primary production in terms of P is realized depends on other, seasonally-dependent, site specific factors such as concentrations of other nutrients, flow velocity, scouring, grazing, transparency, and temperature.

Levels of the dissolved forms of phosphorus were correlated, though not as strongly as particulate P, with streamflow and suspended sediment levels. The influence of stream hydrology on the variability of TDP is not well established. Munn and Prepas (1986), Smith (1976), and Rigler (1979) observed positive correlations between discharge and TDP. However, no significant relationships (Meyer and Likens 1979; Hobbie and

Likens 1973) and negative correlations (Prairie and Kalff 1988b) have also been reported. In the Flathead River, variations in the levels of TDP may result, in part, from adsorbtion/desorbtion of phosphorus from particles suspended in the water column. Dissolution of phosphorus during periods of high streamflow is likely promoted by the high water velocities and turbulence characteristic of these periods. Flushing of phosphorus from groundwater sources can account for up to 20% of the increased TDP on an annual basis (Stanford and Ward 1988). In addition, temperature and solar irradience may play roles in the dynamics of TDP in this system (Prairie and Kalff 1988b).

Monitoring programs for phosphorus in the Flathead River must take into account the marked seasonality of its concentrations and its rapid change with time during the freshet period. Mean concentrations and loads of phosphorus may be underestimated, as freshet peaks will likely be missed, if sampling is limited (ie. n<12/year) and distributed evenly over time. Better estimates will be obtained by sampling more frequently at freshet and less frequently during low flows. However, if too many samples are taken during freshet both the annual concentration means and loads may be over-estimated (see Valiela and Whitfield in press). If the purpose of sampling is to detect violations of specified maximum levels, however, such event-oriented sampling is advantageous.

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KEY WORDS

Phosphorus, temporal variability, water quality monitoring

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