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Seasonality of phytoplankton production in the Columbia River: A natural or anthropogenic pattern?

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Abstract—This study evaluated seasonal variability in the quantity and quality of particulate organic matter exported by the Columbia River into its estuary. Samples of suspended particulate material (SPM), collected monthly over a 1 year period (November 1995–October 1996) from a freshwater site in the Columbia River, near the head of its estuary, were analyzed for total aluminum, particulate organic carbon and nitrogen (POC and PN, respectively) and algal pigments (chlorophyll and carotenoids). High Al content, averaging 7.9% by weight throughout the year, indicated that detrital minerals accounted for the majority of SPM mass at all times. Organic matter (approximately $2 \times$ POC) varied on a seasonal basis both in terms of its mass contribution to SPM (5–26% by weight) and its chemical composition. In winter, organic matter originated mainly from allochthonous sources, most likely from erosion of soils. Diatoms, the major phytoplankton group present as inferred from pigment analysis, “bloomed” in April–June 1996, resulting in increased autochthonous contribution to POC during spring and summer as well as increased organic matter content of SPM introduced to the estuary. Comparison with results for the same site in the mainstem Columbia obtained between 1990 and 1999 as part of a land-margin ecosystem research project shows that enhanced algal production in springtime is not a feature unique to our data set, at least in the Columbia River’s present highly regulated state of hydrographic operation. The possibility is discussed that recent human influence, principally dam construction, has significantly altered the historical SPM concentration and the chemical composition of its associated organic matter. Copyright © 2001 Elsevier Science Ltd

1. INTRODUCTION

The world’s rivers annually deliver $\sim 2 \times 10^{14}$ g of particulate organic carbon (POC) to the coastal ocean (Hedges and Keil, 1995). Mass balance calculations indicate that much of this allochthonous input is not preserved in marine sediments (Ittekkot, 1988; Hedges, 1992; Keil et al., 1997). It is remineralized by biogeochemical processes which are perhaps now all accounted for but certainly not fully understood at a mechanistic level (Aller, 1998; Hartnett et al., 1998). Potential sites of remineralization include hydrodynamically controlled turbidity maxima that form transiently within estuaries (ETM, as per Meybeck et al., 1988; Dyer, 1997) and the zone of sediment dynamics at the surface of deltaic and adjacent coastal deposits (Hedges and Keil, 1995). Although remineralization efficiency in a particular sedimentary setting depends upon an assortment of environmental factors [e.g., redox conditions (Aller, 1994); mixing dynamics (Canfield et al., 1993); physicochemical association of organic matter with particles (Keil et al., 1994)], chemical composition of the riverborne POC is also an important consideration (e.g., Alexander, 1994). There is now good reason to believe that riverborne POC composition, and consequently its metabolic quality, varies significantly between systems and even within given systems on a seasonal basis.

Meybeck (1982) and others (e.g., Ludwig et al., 1996) showed a conspicuous trend relating the fraction of SPM-associated POC to SPM concentration in world rivers (Fig. 1). Organic carbon content, expressed as a weight percentage (%POC) of total suspended particulate material (SPM) mass,

appears highest (i.e., 10–15% or greater) in rivers of lowest turbidity (~ 10 mg SPM/L) and rapidly diminishes to a low level ($\sim 0.5\%$) in rivers of highest turbidity (> 1 g SPM/L). Assuming this trend is not a mathematical artifact (Berges, 1997), two alternative biogeochemical processes could explain it. In rivers where allochthonous POC (e.g., vascular plant litter and soil organic matter) always dominates (“brown” systems), the trend for decreasing %POC versus increasing SPM is caused by a shift from organic-rich vascular plant litter (characteristic of uppermost soil horizons; e.g., Hedges and Oades, 1997) to organic-poor minerals (characteristic of deeper soil horizons; e.g., Hedges and Oades, 1997) as mechanical erosion intensifies. In rivers where significant phytoplankton production can occur (“green” systems), the same %POC versus SPM trend results from variation in the contribution of eroded minerals and its associated organic matter due to factors such as seasonal change in river flow. Although these two explanations differ in detail, both share the fundamental similarity that a decrease in %POC with increasing SPM concentration is caused by a dilution effect that is linked to the intensity of mechanical erosion. Furthermore, both allow for a change in the intrinsic “metabolic quality” of the POC transported downstream and ultimately discharged to the ocean.

It is now possible to cite clear examples of both types of river systems. Extensive evidence shows the Amazon River is a “brown” system (Devol and Hedges, 2000 and references therein), while relatively comprehensive data sets published for the Loire (Meybeck et al., 1988) and St. Lawrence (Pocklington and Tan, 1987) identify these rivers as “green” systems. In order to define what drives the trend between %POC and SPM in a given system, information about POC composition is required. Beyond basic measurements of bulk SPM and POC

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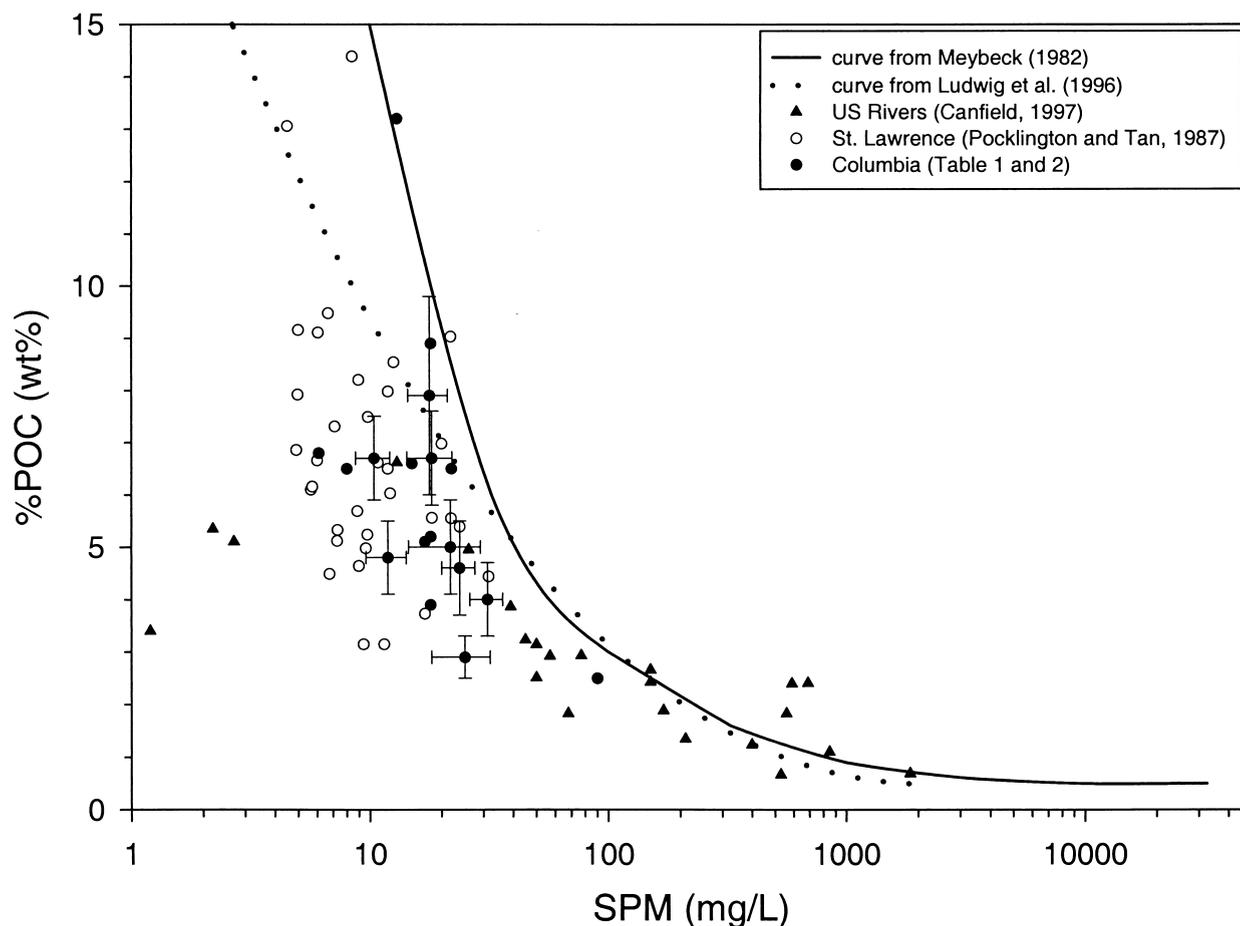


Fig. 1. Empirical relationship between the particulate organic carbon content (%POC, as weight percentage of suspended particulate materials) and SPM concentration in world rivers that was first noted by Meybeck (1982) and more recently refined by Ludwig et al. (1996). Superimposed on these two generalized curves are individual data obtained from analysis of %POC in SPM collected between May and June in 23 rivers throughout the continental United States (Canfield, 1997) and seasonally over multiple years in the St. Lawrence (Pocklington and Tan, 1987) and Columbia (Tables 1 and 2) rivers.

concentrations, such data are yet scarce for most rivers. Results from our study of riverborne POC and its compositional attributes put the Columbia River into perspective with the two possible interpretations of the %POC versus SPM trend documented for the world's rivers (Fig. 1).

The Columbia is the third largest river in the United States in terms of annual freshwater discharge to the oceans (van der Leeden et al., 1990). It drains a 660,000 km² watershed which includes portions of six US states and one Canadian province (Fox et al., 1984). Along its entire length, the river has been altered dramatically from its natural condition through dam construction, irrigation projects and dredging operations in shipping channels (Harden, 1996). These alterations have resulted in highly regulated flow and significant dampening of the seasonal range in freshwater discharge. Today, water in the Columbia River has relatively low turbidity (~10–30 mg SPM/L; Prahl et al., 1997; 1998) when gauged on the scale of the world's rivers (10 to >10³ mg SPM/L; Berner and Berner, 1996). However, historical data indicate that SPM concentrations in the pre-dam Columbia River were perhaps twice what they are today (van Winkle, 1914). It is believed that the addition of dams has caused the observed turbidity reduction,

and therefore reduced delivery of SPM to the Columbia River estuary and its adjacent coastal margin (Sherwood et al., 1990).

Results presented in this paper show that autochthonous phytoplankton production best accounts for seasonally elevated %POC in suspended particulate material discharged by the Columbia River to its estuary and adjacent coastal environment. An argument is developed that the addition of an extensive, interconnected network of dams on the Columbia and its major tributaries has not only reduced turbidity, but significantly changed the organic composition of SPM discharged by this river. That is, suspended organic matter in the Columbia has either shifted from "brown" to "green" or, at the very least, has become "greener" than it would have been naturally owing to significant reduction in turbidity and increase in water retention time behind the network of impoundments created by these dams.

2. METHODS

Water samples were collected approximately monthly from November 1995 until October 1996 in cooperation with the US Geological Survey's (USGS) National Stream Quality Accounting Network (NASQAN) project (Portland, OR). The sampling site in the Columbia

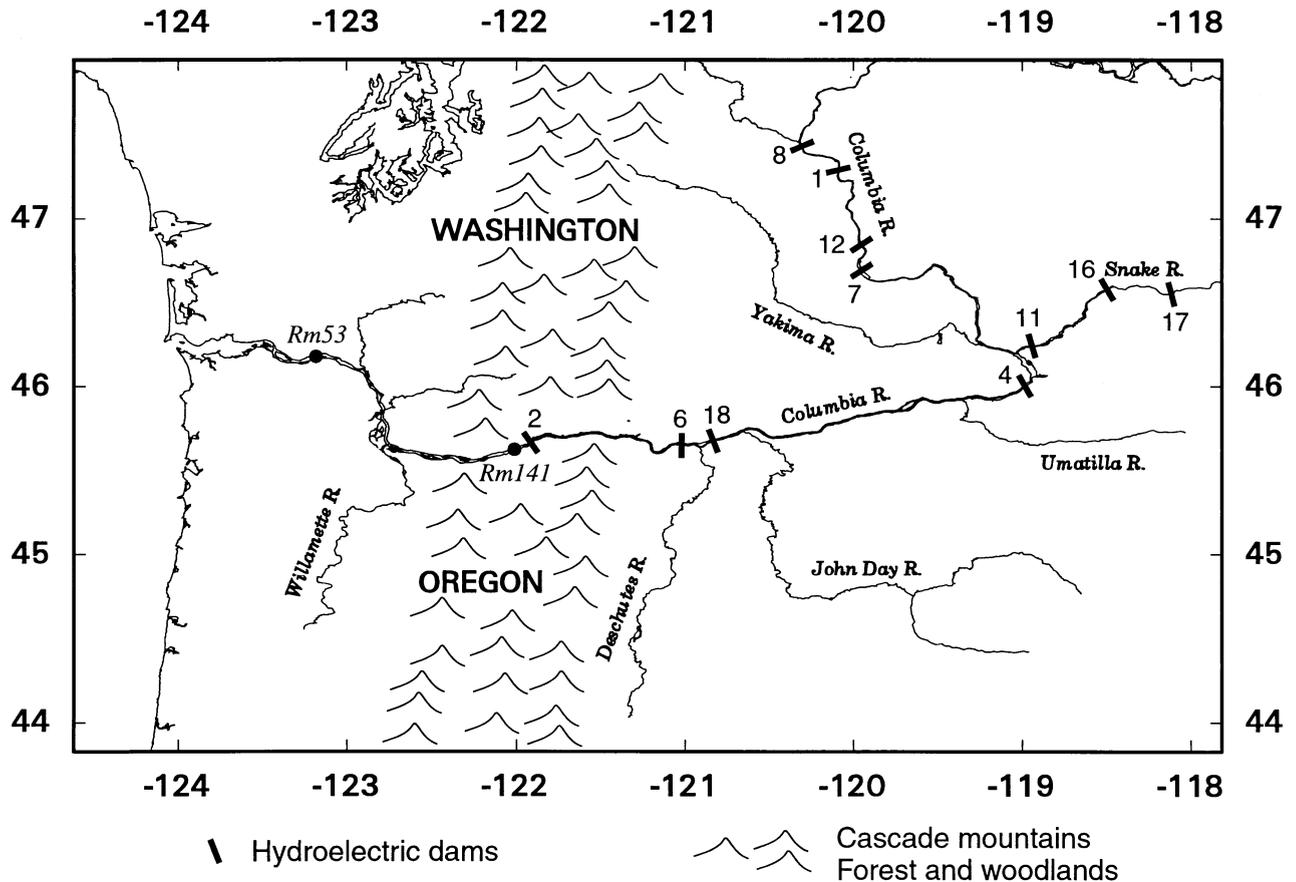


Fig. 2. Map of the lower Columbia River drainage showing the location of the site (Rm53) sampled monthly in this study. A second site in the mainstem Columbia River (Rm141), located just below Bonneville Dam and monitored historically by the USGS (Portland District) for various water quality purposes, is also identified. The locations of the 11 major dams now present in the portion of the Columbia River–Snake River system shown are also indicated. The number associated with each mark identifies the specific dam of the 21 major structures in the overall Columbia River–Snake River system (Dietrich, 1995) that each represents: (1) Rock Island (1933); (2) Bonneville (1938); (4) McNary (1957); (6) The Dalles (1960); (7) Priest Rapids (1961); (8) Rocky Reach (1961); (11) Ice Harbor (1962); (12) Wanapum (1964); (16) Lower Monument (1970); (17) Little Goose (1970); (18) John Day (1971).

was located 85 km upstream from the mouth at the Beaver Army Terminal near Quincy, OR (46°10.90'N, 123°10.97'W; Fig. 2). This site is identified as river mile 53 (Rm53) in subsequent discussion to maintain consistency with prior convention and use of this code on navigational charts. Rm53 is ideal for obtaining representative samples of SPM entering the estuary, as it is the first upstream location where the river channel is narrow (~650 m), uninterrupted by islands and, therefore, geometrically well constrained.

Sampling technique. Collection was performed with the goal of generating one bulk water sample for each monthly time point representing a flow-weighted cross section of the river. This goal was accomplished by combining samples collected by a small boat from five equally spaced locations across the river. At each location, a depth-integrated sampler fitted with an 8 L collapsible Teflon bag and Teflon nozzle was lowered to the bottom and then raised back to the surface, collecting water isokinetically, and yielding a velocity-weighted sample (Edwards and Glysson, 1988). The sampling process took ~2 h and 3–10 L of water were collected, depending upon river flow rate. The water sample in a 10 L Nalgene carboy surrounded by ice was transported within 2–3 h to Oregon State University (OSU). At OSU, the contents of the carboy were homogenized by shaking, and water aliquots were withdrawn immediately for various analyses.

Gravimetric and elemental analyses. The gravimetric weight of SPM was determined by pressure filtering (nitrogen gas, 10–15 psi) a known volume (0.5–2 L) of each bulk water sample through preweighed

polycarbonate membranes (1.0 μm pore size, 90 mm diam.; poretics). The filters were oven-dried (24 h at ~50°C) and reweighed, allowing for the determination of SPM concentrations (mg/L).

Total aluminum content of SPM on these filters was then measured by nondestructive instrumental neutron activation analysis (INAA). Irradiation of the sample in the 1 megawatt TRIGA reactor at OSU produced a short-lived radioisotope for this element (^{28}Al , 2.24 min half-life). The samples, after a short decay period (5 min), were then counted for Al ($\pm 0.5\%$ uncertainty) using a high resolution Ge(Li) detector coupled to a multichannel analyzer. Total Al content of each sample was calculated using USGS rock standards as internal checks on accuracy. Further details of the INAA procedure are found elsewhere (Collier, 1991).

SPM on the polycarbonate membrane filters used for total Al analysis were subsequently analyzed for biogenic silica (BSi) content after a period of ~1 year had elapsed, allowing for complete decay of short-lived, artificial isotopes produced by INAA. BSi was measured by leaching filters in a hot (85°C) alkaline solution (1% Na_2CO_3) over a 5 h period. Subsamples of the leachate were removed at 3, 4, and 5 h and analyzed for dissolved silicate concentration. A least-squares regression with extrapolation to the intercept was made to determine the BSi concentration and to compensate for concurrent dissolution of mineral silicates (DeMaster, 1981). The precision of this analysis is typically $\pm 10\%$ (1σ) or better.

Samples for particulate organic carbon (POC) and nitrogen (PN)

were obtained by vacuum filtering (≤ 200 mm Hg) water (50–250 mL) through precombusted (450°C, ~ 4 h) glass fiber filters (nominally 0.8 μm pore size, 25 mm diam., Whatman GF/F). The filters were folded, placed in precleaned borosilicate vials with Teflon-lined caps and stored at -15°C . Immediately prior to analysis, frozen samples were removed from the vials, fumed with concentrated hydrochloric acid (~ 4 h) to remove any inorganic carbon (Hedges and Stern, 1984) and then oven-dried (24 h at $\sim 50^\circ\text{C}$). The dried filters were packed into solvent-cleaned tin boats and analyzed on a Carlo Erba NA-1500 elemental analyzer using acetanilide as a calibration standard (Verardo et al., 1990). The precision of triplicate filter analyses was $\pm 3\%$ (1σ) or better.

Phytoplankton pigment analyses. SPM samples for algal pigment determination were isolated by vacuum filtering (≤ 200 mm Hg) water (50–250 mL) through precombusted glass fiber filters (nominally 0.8 μm pore size, 25 mm diam., Whatman GF/F). The filters were then either folded in aluminum foil packets and stored in liquid nitrogen or analyzed immediately. To determine pigment concentrations, each filter was cold extracted (-15°C) in a polypropylene centrifuge tube using 90% acetone (5 ml, 12–24 h). The colored extracts were then centrifuged in preparation for pigment analysis.

The high performance liquid chromatographic (HPLC) method (Wright et al., 1991) with slight modification of the solvent program (Sullivan, 1997) was employed for analysis of phytoplankton pigments in sample extracts. Chromatographic separations were made using a Perkin-Elmer Series 400 solvent pump equipped with an injection loop (100 μl), a Beckman Ultrasphere column (5 μm octadecylsilane beads, 4.6 mm \times 15 cm) and a dual wavelength, ultraviolet (UV)-visible detector (Thermoseparation Products SpectraSystem UV2000). Dual wavelength detection at 436 nm and 665 nm allowed for clear differentiation between carotenoid and chlorophyll chromatographic peaks. Quantification was accomplished by comparison of integrated peak areas obtained by commercial chromatographic software (LabCalc, Galactic Industries Corporation) with those obtained for external standards. Chlorophyll *a* (Sigma Chemicals), chlorophyll *b*, fucoxanthin, and zeaxanthin (courtesy of R. Bidigare) dissolved in 100% acetone were used as the external calibration standards. The precision of triplicate filter analyses was typically ± 5 –10% (1σ).

Chlorophylls were also measured by the fluorometric method of Strickland and Parsons (1972) using a Turner Designs fluorometer and the equations defined for chlorophyll *a* and pheophytin *a* quantification by Conover et al. (1986). Authentic chlorophyll *a* (Sigma Chemicals) and pheophytin *a* (acidified chlorophyll *a*) were used as standards for calibration of the fluorometer. The precision of triplicate filter analyses was typically $\pm 10\%$ (1σ).

Comparison shows measurements of chlorophyll *a* concentration by the fluorometric method correlated well with those obtained by HPLC ($r^2 = 0.97$) but were consistently higher by $\sim 20\%$ (Fig. 3A). Pheopigment results showed poorer correlation ($r^2 = 0.30$) with values by the fluorometric method averaging 6.3 times higher than those obtained by HPLC (Fig. 3B). The cause for this disparity is attributed to interfering fluorescence from other chlorophylls (*b* and *c*) in the fluorometric method (Sullivan, 1997).

All chlorophyll data from past land-margin ecosystem research (LMER) studies of the Columbia River (Simenstad et al., 1994) were obtained by the fluorometric method. In order to quantitatively intercompare results, all values shown graphically for Chl *a* concentration and Chl *a*/POC ratios from LMER samples were multiplied by a factor of 0.80 prior to plotting. This data transformation corrects for the systematic difference noted between the fluorometric and HPLC methods of chlorophyll analysis (see Fig. 3).

3. RESULTS

SPM concentration variation. SPM concentrations at Rm53, measured approximately monthly between November 1995 and October 1996, varied by well over an order of magnitude (i.e., 6 to 90 mg/L; Table 1). By far, the highest concentration occurred during a major flood event in February 1996. If the flood sample is excluded from consideration, however, the range of variability is narrowed to less than a factor of 4 (i.e.,

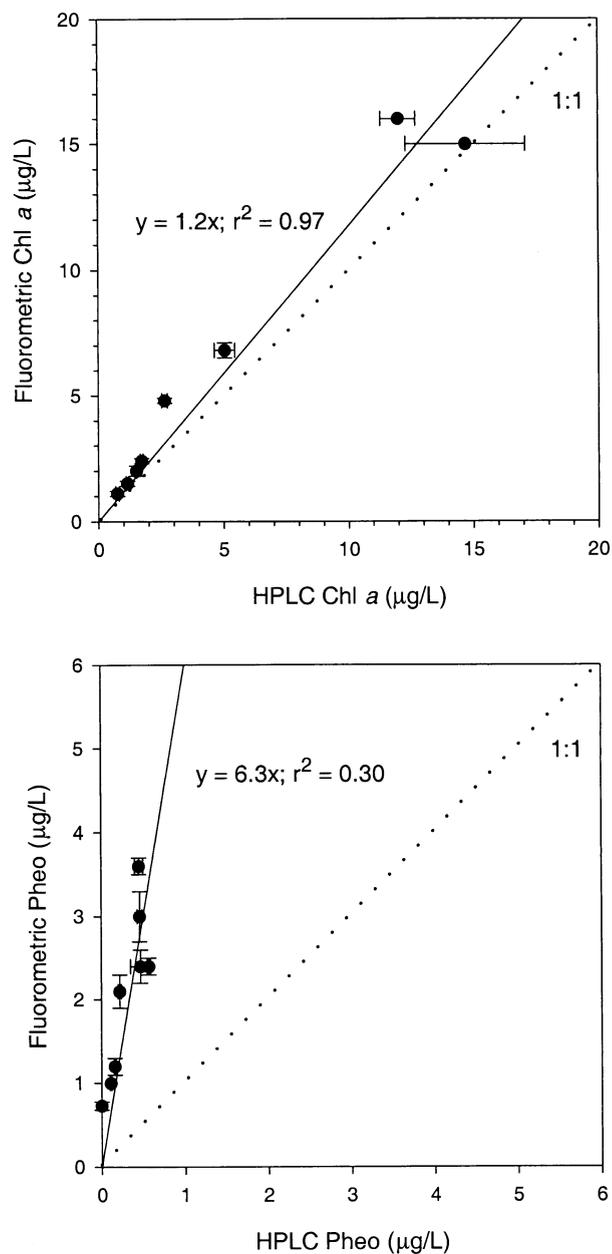


Fig. 3. Intercomparison of chlorophyll *a* and pheopigment concentrations determined by high performance liquid chromatography (HPLC) and fluorometry for replicate samples collected at Rm53 between November 1995 and October 1996. Best-fit lines and their statistics from type I linear regression analysis of each data set are indicated on the graphs. Regression analyses were performed assuming that HPLC determinations of chlorophyll *a* and pheopigment concentrations are accurate benchmarks while the fluorometric determinations are uncertain owing to interference problems (see experimental methods for more detail).

6 to 22 mg/L). Variability in this 1 year data set for SPM concentration does not appear random; SPM concentration displays a slight, direct proportional increase ($r^2 = 0.57$) with river flow rate (Fig. 4). Although seasonal variability of SPM at given river flow is evident in the LMER data (Table 2; Fig. 4), there are not enough repetitive samples at Rm53 in any of the LMER years (1990–1999) to either support or refute a direct

Table 1. Summary of compositional data obtained for suspended particulate materials (SPM) collected at Rm53 in the lower Columbia River over a 1 year period in 1995–1996.

Collection date	River flow (m ³ /s)	SPM (mg/L)	Al (wt.%)	BSi ^a (wt.%)	%POC (wt.%)	C/N (mole ratio)	Chl <i>a</i> (μg/L)	%Chl <i>a</i> ^b	Chl <i>a</i> /POC (mg/g)
11/28/95	10,700	22	8.3	5.5	6.5%	13.7	1.5	73%	1.0
1/10/96	10,300	17	8.6	6.5	5.1%	15.0	0.7	100%	0.9
2/14/96	16,700	90	10.1	3.9	2.5%	11.8	1.7	91%	0.8
3/12/96	11,200	18	9.0	6.4	3.9%	9.3	1.2	92%	1.6
4/9/96	7,400	13	7.6	8.7	13.2%	8.6	14.7	97%	8.5
5/14/96	7,800	18	7.4	11.7	8.9%	11.0	19.8	95%	12.7
6/18/96	12,500	15	7.4	7.6	6.6%	10.2	8.6	96%	8.8
7/9/96	8,200	18	6.3	11.3	5.2%	8.5	12.0	96%	12.9
8/27/96	4,800	8.0	7.1	10.2	6.5%	8.6	5.0	92%	9.7
10/23/96	4,900	6.1	7.5	13.2	6.8%	6.1	2.6	92%	6.4

^a Biogenic silica (units of SiO₂).

^b %Chl *a* proportion of chlorophyll *a* to total pigment (chlorophyll *a* plus pheopigment) × 100.

relationship between SPM concentration and flow rate over an annual cycle. However, there is a general proportional increase with river flow when all LMER years are viewed concurrently (although with greater scatter than in our 1995–1996 study period).

Inorganic characteristics of SPM. Total aluminum content (%Al) in SPM was high year round, averaging 7.9% (±1.1%) by weight (Table 1). This value is greater than the continental average for Al in riverborne SPM (6.9 wt.%), but falls within

a range reported for high-runoff rivers (Canfield, 1997). High runoff is equated with increased severity of chemical weathering of rocks, which leaches soluble components (e.g., Ca²⁺, K⁺, Mg²⁺, Na⁺) and leaves lattice-bound elements such as Al enriched in the residual solid. Given that the aluminum content of world average crustal rocks is 8.2 wt.% (Taylor, 1964), the high %Al measured year round at Rm53 indicates that detrital minerals represent, regardless of sampling time, the major contributor to total SPM at that location.

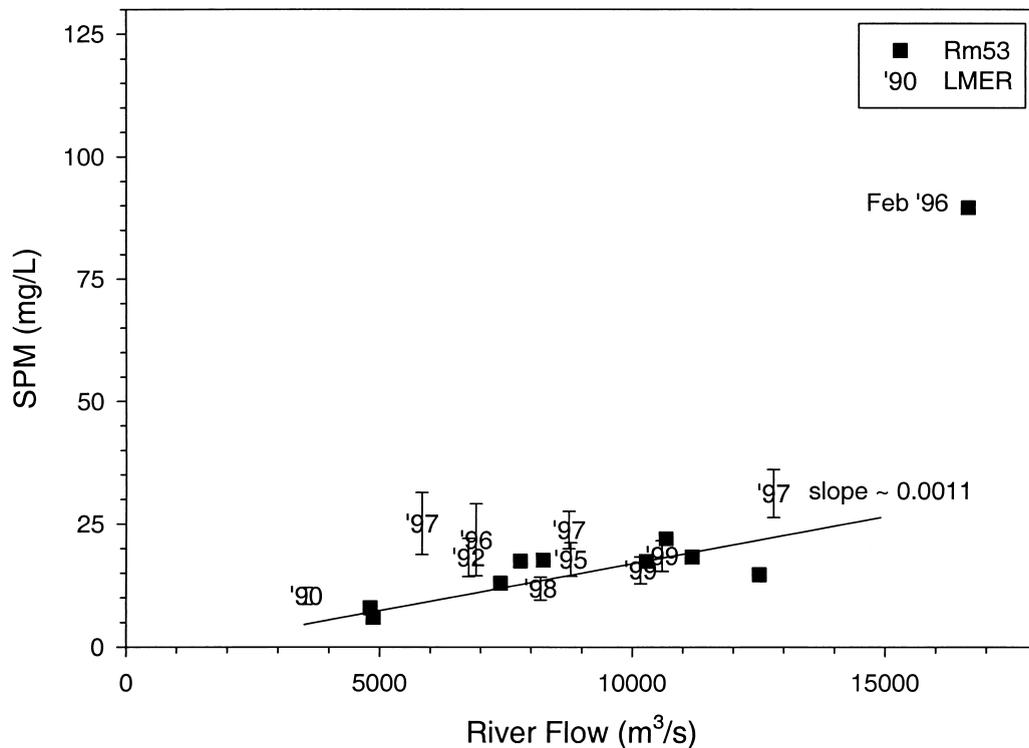


Fig. 4. Scatter plot showing the direct relationship observed between SPM concentration and water discharge at Rm53 during our study period. The point falling farthest off the line corresponds to a sample taken during a major flood event in February 1996. Data obtained between 1990–1999 as part of an LMER project are also plotted (symbol identifies collection year; see Table 2). Error bars on LMER data depict tidal variation ($\pm 1\sigma$) about the mean of measurements made every 2 h over a 12 to 24 h sampling period.

Table 2. Summary of compositional data obtained for suspended particulate materials (SPM) collected at Rm53 in the lower Columbia River at various times between 1990 and 1999 as part of a land-margin ecosystem research (LMER) project (<http://depts.washington.edu/cretmweb/CRETM.html>). Data are tabulated as an average value ($\pm 1\sigma$) for sets of samples collected on each date every 2 h over a 12–24 h period. River flow data were obtained from the USGS (<http://waterdata.usgs.gov>).

Collection date	River flow (m ³ /s)	SPM (mg/L)	%Al (wt.%)	POC (mg/L)	%POC (wt.%)	Chl <i>a</i> (μg/L)	Chl <i>a</i> /POC (mg/g)	C/N (mole ratio)
2/21/98	8180	11.9 ± 2.3	8.6 ± 0.2	0.56 ± 0.02	4.8 ± 0.7	13 ± 1.0	24 ± 2.0	10.4 ± 0.2
5/1/95	8790	17.8 ± 3.4	6.7 ± 0.4	1.4 ± 0.1	7.9 ± 1.9	25 ± 2.0	18 ± 1.6	9.1 ± 0.6
5/10/97	12800	31.2 ± 4.9	7.4 ± 0.8	1.2 ± 0.1	4.0 ± 0.7	9.5 ± 2.1	7.8 ± 1.7	10.3 ± 0.6
5/17/92	6760	18.2 ± 3.9	5.6 ± 0.5	1.2 ± 0.2	6.7 ± 0.9	50 ± 6.8	42 ± 7.4	7.6 ± 0.6
6/12/92	5800			1.2 ± 0.2		32 ± 3.3	27 ± 3.6	8.3 ± 0.3
6/16/99	11200	15.6 ± 2.7		0.73 ± 0.14	4.8 ± 1.2	18 ± 3.0	24 ± 4.4	8.5 ± 0.6
6/22/99	10300	18.5 ± 3.1	6.3 ± 1.4	0.79 ± 0.05	6.5 ± 0.3	20 ± 1.7	26 ± 3.5	9.6 ± 0.3
7/7/97	8750	23.8 ± 3.8	6.7 ± 1.1	1.1 ± 0.1	4.6 ± 0.9	25 ± 1.4	24 ± 3.6	8.5 ± 0.3
7/8/91	7910			1.1 ± 0.1		22 ± 1.6	20 ± 2.5	8.6 ± 0.8
7/19/96	6910	21.8 ± 7.3	7.2 ± 0.6	1.0 ± 0.2	5.0 ± 0.9	19 ± 0.7	19 ± 3.0	7.9 ± 0.4
8/1/91	4920			0.93 ± 0.14		20 ± 3.7	21 ± 4.1	8.1 ± 0.5
9/22/90	3560	10.4 ± 1.7	6.6 ± 0.2	0.62 ± 0.10	6.7 ± 0.8	12 ± 1.5	19.7 ± 3.5	8.0 ± 0.8
10/6/97	5830	25.1 ± 6.9	7.5 ± 0.8	0.73 ± 0.20	2.9 ± 0.4	7.2 ± 0.5	9.5 ± 2.4	10.0 ± 0.8
10/23/90	4460			0.45 ± 0.06		5.3 ± 0.3	12 ± 1.6	7.9 ± 0.8

Throughout winter (i.e., December–March), total aluminum content of SPM remained equal to or greater than the crustal average for this element. Greatest %Al was measured during the February flood event when SPM concentrations were anomalously high. In April, %Al dropped significantly below the crustal average and remained so throughout the following spring, summer, and early fall (Fig. 5A). Similar results were obtained in the LMER data from different years between 1990 and 1999. Although a simple shift in the type of mineralogical input to the river could explain the elevated %Al measured in the February flood sample, this process alone cannot account for the conspicuously reduced values observed after April. Further chemical characterization of the SPM shows that dilution of mineral mass with biogenic particles produced within the river system best explains the depression of %Al below the crustal average during this time period.

Biogenic characteristics of SPM. Organic matter content, assessed from POC measurements, contributes to SPM mass; however, this contribution at Rm53 was not constant through time (Table 1; Fig. 5B). The POC content of SPM varied significantly from a low of 2.5% in the February flood sample to a high of 13.2% in early spring. Humic materials, which comprise a major fraction of sedimentary organic matter, are ~50% carbon by weight (e.g., Ertel and Hedges, 1984); thus, the quantity of organic matter calculated with this conversion factor accounts for only 5% of SPM mass during the February flood event but as much as 26% at specific times in spring and summer—the period when %Al fell consistently beneath its crustal average. Given that the organic carbon content of soils in the Willamette River basin lies in a range of 1.4–4.3% by weight (Sollins et al., 1984; Prahl et al., 1994) and values in any soil rarely exceed 5% by weight unless waterlogging occurs (Hedges and Oades, 1997), erosional input of soil could conceivably account for all organic matter present in the February flood sample but only a fraction of that measured at other times of the year (Fig. 5B).

Chlorophyll *a* (Chl *a*) data show that in addition to quantity, the quality (chemical composition) of organic matter content in this set of SPM samples changed significantly throughout the year. Chl *a* concentrations were uniformly low (≤ 1 – 2 μg/L) in

winter, including during the February flood event when SPM levels were anomalously high (90 mg/L, Fig. 4), and increased significantly in the spring, reaching a maximum of 19.8 μg/L in May (Fig. 6A). The LMER data for Chl *a* follow a similar pattern, with the exception of May 1992 when a large phytoplankton bloom was documented in the river (Small and Morgan, 1994), and May 1997 when high flow rate apparently reduced Chl *a* concentration in the face of enhanced SPM concentration (Table 2).

A parallel seasonal pattern is apparent if chlorophyll *a* data are normalized to organic carbon (i.e., Chl *a*/POC, Fig. 6B). Both measured and empirically predicted Chl *a*/POC values (e.g., Harris, 1986; Riemann et al., 1989; Meybeck et al., 1988) for healthy phytoplankton fall in the range of 10–30 mg/g and allochthonous sources contain no measurable chlorophyll *a*. Given these endmember constraints, a major fraction of the elevated POC content from spring through fall appears to be derived from phytoplankton produced within the Columbia River drainage system. In contrast, the presence of chlorophyll-poor POC associated with SPM in winter time and in the May 1997 LMER data, is consistent with soil-dominated contribution to riverborne organic matter at those times.

Mole ratios of total organic carbon to nitrogen (C/N) are often employed to distinguish relative organic contribution from terrestrial (soils, vascular plant debris) and aquatic (phytoplankton) sources to sedimentary materials (Hedges et al., 1997 and references therein). Typical C/N values for pure soil organic matter (>10) and vascular plant debris (>20), in particular, are systematically higher than those for freshwater phytoplankton (~6.7). Consequently, natural SPM samples containing an admixture of material from such sources should display intermediate C/N values reflective of their weighted contribution. Given this parametric response, the overall seasonal pattern for C/N corroborates salient conclusions just made from interpretation of Chl *a*/POC results (Fig. 6C). SPM in winter time contained organic matter characteristic of local soils (C/N: 11.1–13.7; Prahl et al., 1994), while at the onset of spring, C/N values decreased and approached those expected for average, freshwater phytoplankton.

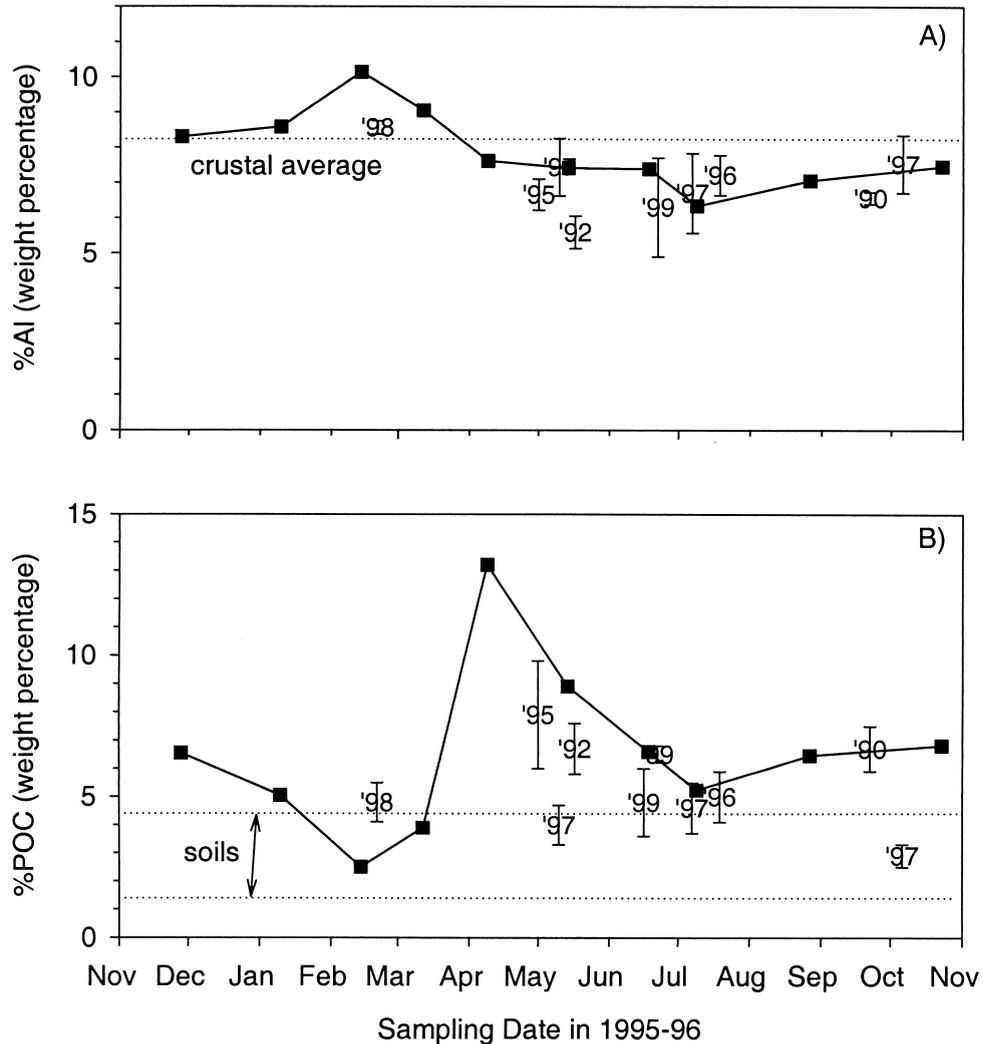


Fig. 5. Time series record for weight percentage (A) aluminum (%Al) and (B) particulate organic carbon (%POC) measured in SPM collected approximately monthly at Rm53 during our study period. The horizontal dotted line in plot (A) depicts the Al content (8.2%) reported for average crustal rocks (Taylor, 1964). The horizontal dotted lines in (B) depicts the range of organic carbon content measured in various soils from the Willamette valley (1.4–3.5%; Prahll et al., 1994). Data for each parameter obtained between 1990–1999 as part of an LMER project are also plotted (mean $\pm 1\sigma$, symbol identifies collection year, see Table 2).

Riverborne phytoplankton community composition. %Chl *a* [$\equiv \text{Chl } a / (\text{Chl } a + \text{Pheo}) \times 100$] represents an index of phytoplankton “freshness” (Small and Morgan, 1994), where Chl *a* and Pheo are, respectively, the concentration of chlorophyll *a* and the sum of all pheopigments found in a given HPLC trace. In all cases, pheopigments were detected almost entirely as pheophytin *a*. With the possible exception of the sample collected in November 1995, minimal levels of pheopigments were detected (i.e., %Chl *a* $\geq 90\%$, Table 1). Given such high %Chl *a* values, the phytoplanktonic component of organic matter in essentially all samples at Rm53 appears associated predominantly with intact, viable cells rather than with moribund cells and algal detritus.

Results from detailed pigment analyses by HPLC indicate that diatoms were the dominant phytoplankton group present at all sampling times during the year. Fucoxanthin, a chemotaxo-

nomic marker for diatoms (Goodwin, 1971), was by far the most abundant carotenoid observed (Sullivan, 1997). Furthermore, values for the concentration ratio of fucoxanthin to chlorophyll *a* (Fuco/Chl *a*) all fell near, and often within, the range characteristic of pure diatom cultures (Fig. 7). Carotenoid markers (Goodwin, 1971) for green algae (chlorophyll *b*), cryptophytes (alloxanthin), and blue-green algae (zeaxanthin) were also detected in the samples, but in very low concentrations both absolutely and relative to chlorophyll *a*. Hence, contribution from these groups to the overall phytoplankton standing stock would appear minor (Sullivan, 1997). This interpretation of results from HPLC analyses agrees with microscopy-based taxonomic generalizations made previously about phytoplankton assemblages in the lower Columbia River during late spring to early fall months (Rickert et al., 1977; Neitzel et al., 1982; Lara-Lara et al., 1990).

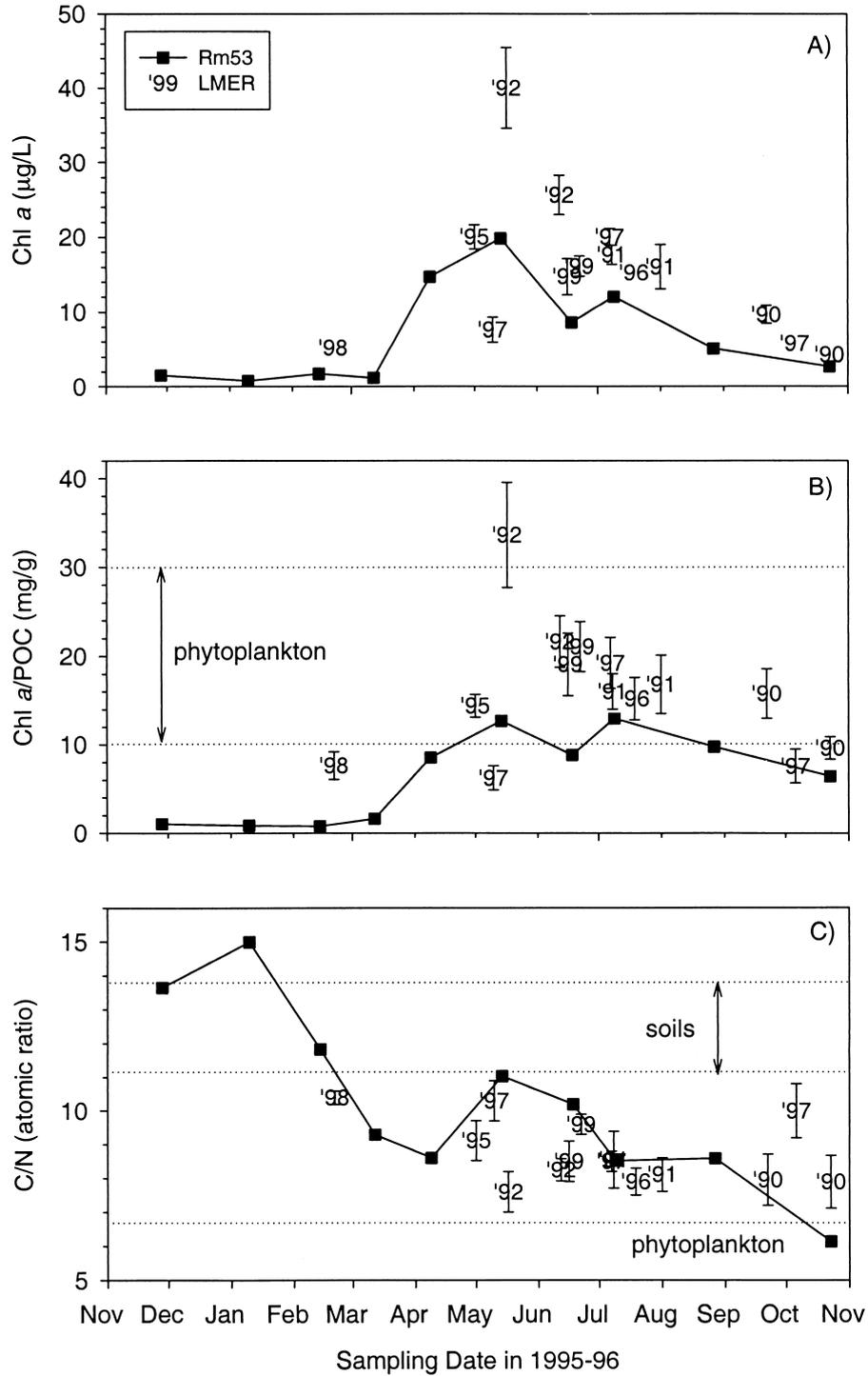


Fig. 6. Time series record for (A) chlorophyll *a* concentration (Chl *a*, µg/L), (B) the chlorophyll *a* content of POC (Chl *a*/POC), and (C) the particulate organic carbon to nitrogen (C/N) composition of SPM measured in river waters collected approximately monthly at Rm53 in the mainstem Columbia River. Horizontal dotted lines in (B) depict the typical range for Chl *a*/POC values measured in healthy phytoplankton cells from cultures and field collection (10–30 mg/g; Harris, 1986; Meybeck et al., 1988; Riemann et al., 1989) while those in (C) bracket the range of C/N reported for soils from the Willamette valley (11.4–13.7; Prahl et al., 1994) and depict average phytoplankton composition (~6.7). Data for each parameter obtained at Rm53 between 1990–1999 as part of an LMER project are also plotted (mean ± 1σ, symbol identifies collection year, see Table 2).

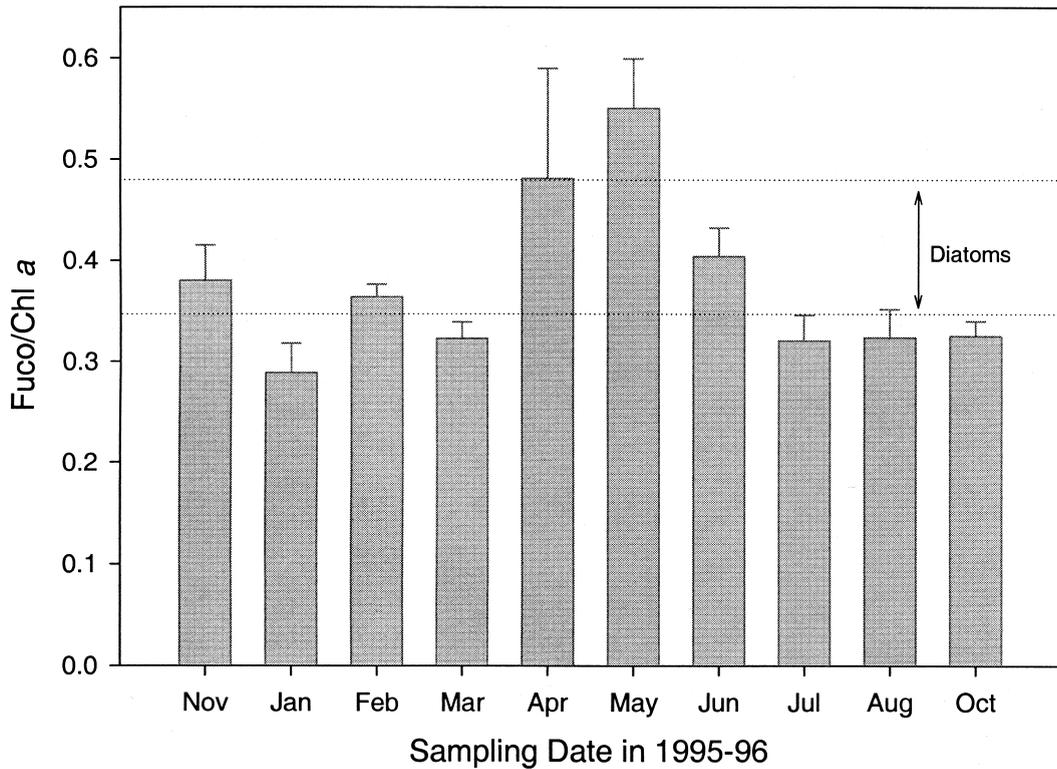


Fig. 7. Time series record for values of the fucoxanthin to chlorophyll *a* (Fuco/Chl *a*) ratio ($\pm 1\sigma$) measured in SPM throughout the year at Rm53. Horizontal dotted lines depict the range of Fuco/Chl *a* values measured in pure diatom cultures (Sullivan, 1997 and references therein).

The importance of diatom production as a contributor to SPM mass is further corroborated by measurements of biogenic silica (BSi). BSi (in units of SiO_2) content of SPM ranged from 3.9 to 13.2 wt.% (Table 1). The lowest value was measured during the February flood, a period when POC and algal pigment concentrations were also minimal. A broad maximum was observed beginning in late spring and extended through the remaining time series, the period when significant autochthonous diatom production was inferred by results from algal pigment and elemental (i.e., POC, C/N) analyses. Although correlation between BSi and POC concentration was not strong ($r^2 = 0.57$), BSi/POC spans a range of values (0.3–1.0) not too unlike that expected for freshwater diatoms (1.8 ± 1.0 ; Conley et al., 1989). Furthermore, simple linear regression analysis shows that the weight percentage of BSi and Al% are inversely correlated ($\text{Al}\% = 10.4 - 0.30 \text{ BSi}$, $r^2 = 0.66$). Given these results, it is clear that these chemical signals derive from distinct, independent sources—BSi from diatom frustules and total aluminum from the lattice structure of detrital minerals.

4. DISCUSSION

Interannual variability in the lower Columbia. Comparison of LMER data collected in discrete months between 1990–1999 (Table 2) with those from the present study not only reveals the degree of interannual variation in SPM concentration and chemical composition in this river system, but also

provides insight to the potential cause(s) for interannual variability.

In all LMER field work, SPM concentrations measured at Rm53 fell within a narrow range ($\sim 10\text{--}30 \text{ mg/L}$) consistent with observations made in our 1995–1996 study except during the period of the February flood. The increased scatter in the LMER data may have resulted, at least in part, because isokinetic cross-channel sampling was not employed during the LMER project. Rather, LMER samples were collected from mid-depth in the water column at a fixed site near the edge of the river channel. Therefore, the LMER samples are likely less representative of average SPM concentration transported through the channel cross section at Rm53.

Nonetheless, the chemical composition of SPM collected in the LMER project varied as a function of sampling time, and the variation of each chemical property followed a seasonal pattern like that documented by our 1995–1996 time series (with May 1992 and 1997 often the exception). Aluminum values approximated the crustal average ($\sim 8.2 \text{ wt.}\%$) in winter and were consistently depressed below this benchmark in spring through fall (Fig. 5A). As observed in our study, %Al values in the LMER data set tended to vary inversely with the organic matter content of SPM (Figure 5B) and, with the phytoplankton contribution to organic matter content (Figs. 6A–6C). Dilution of detrital mineral mass with phytoplankton biomass (i.e., organic matter and biogenic silica) best accounts for the observed seasonal behavior in %Al. Phytoplankton production is an annual spring time phenomenon in the modern

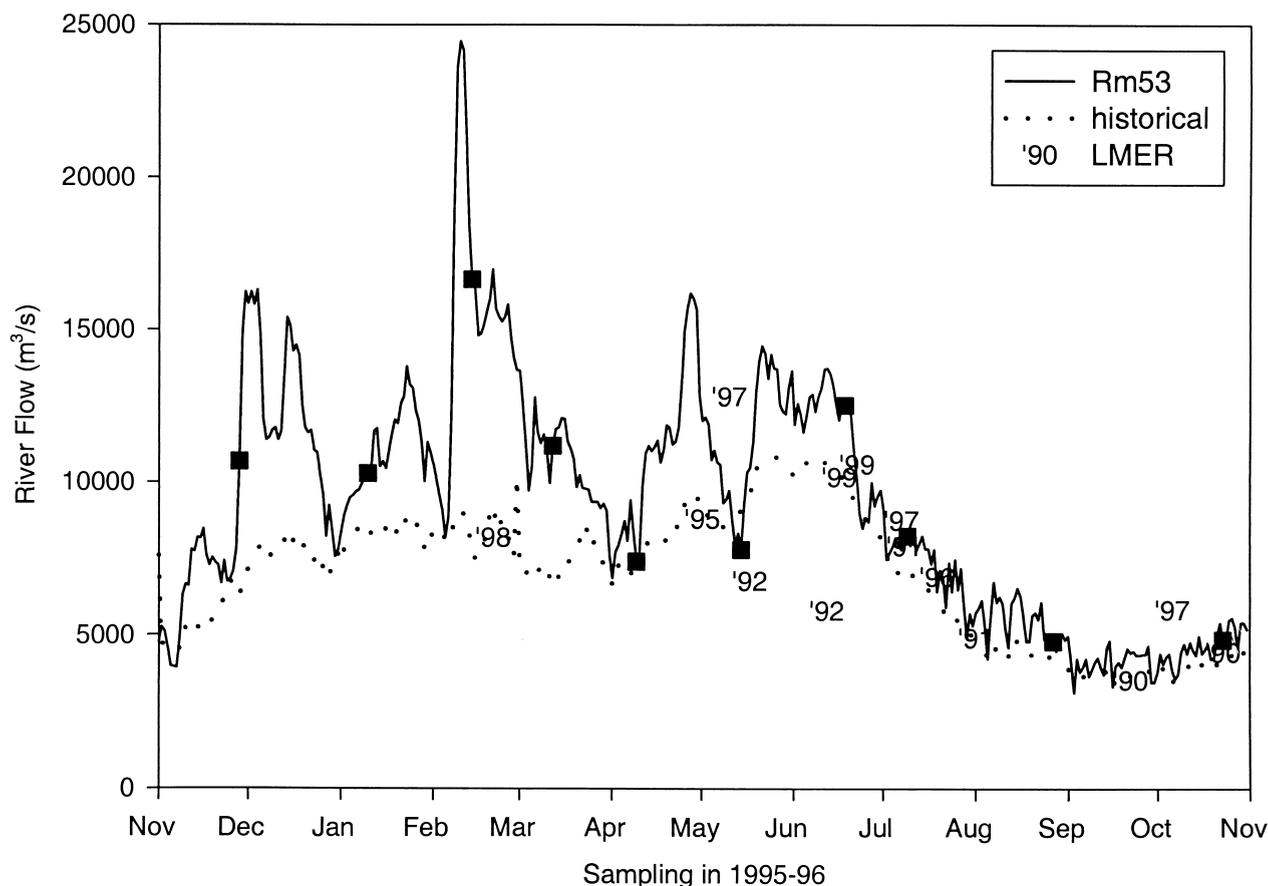


Fig. 8. (A) Daily water discharge record for Rm53 spanning the time frame of November 1995 to October 1996. Filled squares identify times when samples were collected at Rm53 as part of this study. Year symbols depict river flow when samples were collected at Rm53 between 1990–1999 as part of an LMER project (see Table 2). Historical record for water discharge at Rm53, obtained by averaging daily measurements for all available water years from 1968–1995 (USGS data, <http://waterdata.usgs.gov>), are also plotted for comparison.

Columbia River and accounts for the majority of POC associated with SPM from spring to early fall.

Further inspection of the combined data set shows an inter-annual variation of POC content and composition. As indicated earlier, interannual variability is most apparent during the “spring freshet” period which typically occurs in the Columbia River drainage from May until June as a consequence of enhanced snowmelt. For example, when the “spring freshet” was virtually absent in May to June 1992 (Fig. 8) due to an unseasonably dry winter, SPM was rich in POC (~6.9 wt.%, Fig. 5B) and organic matter displayed the most phytoplankton-like characteristics of any time sampled (Figs. 6A–6C). Conversely, when samples were collected during a particularly strong “spring freshet” in May 1997 (Fig. 8), organic matter composition bore characteristics more intermediate between phytoplankton and soil (Figs. 6A–6C). Thus, phytoplankton within the river appears tied to flow rate, or at least to extremes in flow rate.

Flow rate governs the dynamics of vertical mixing in the water column and thereby can exert some control over light availability to phytoplankton. Frey et al. (1983) and Lara-Lara et al. (1990) identified light availability as the primary controlling factor for phytoplankton production in the river and estu-

ary. River flow also controls retention time of water in the drainage basin and consequently phytoplankton lifetime in the river system. As flow increases, phytoplankton have less time to grow as they are more rapidly exported from the river to its estuary and adjacent continental margin (as in May 1997). The reverse appears to be true in May 1992.

Although flow seems to have some impact on phytoplankton growth, classical oceanography and limnology have taught us that phytoplankton production within the river must also bear some linkage to nutrient availability. Nitrate, phosphate, and silicate concentrations are always measurable in the river and display large, synchronized seasonal cycles with highest values observed in winter, lowest in late summer (Fig. 9). The seasonal pattern of variation in nutrient concentration for our sampling period in 1995–1996 parallels a longer-term historical record for the lower Columbia River (1978–1994) with the greatest difference evident for phosphate. Cursory interpretation would ascribe the nutrient drawdown in summer to the effect of phytoplankton production. Based on Redfield stoichiometric considerations of ~16N:1P, the nutrient most likely in limiting supply for any type of phytoplankton growth would appear to be phosphate. Yet, there is always detectable phos-

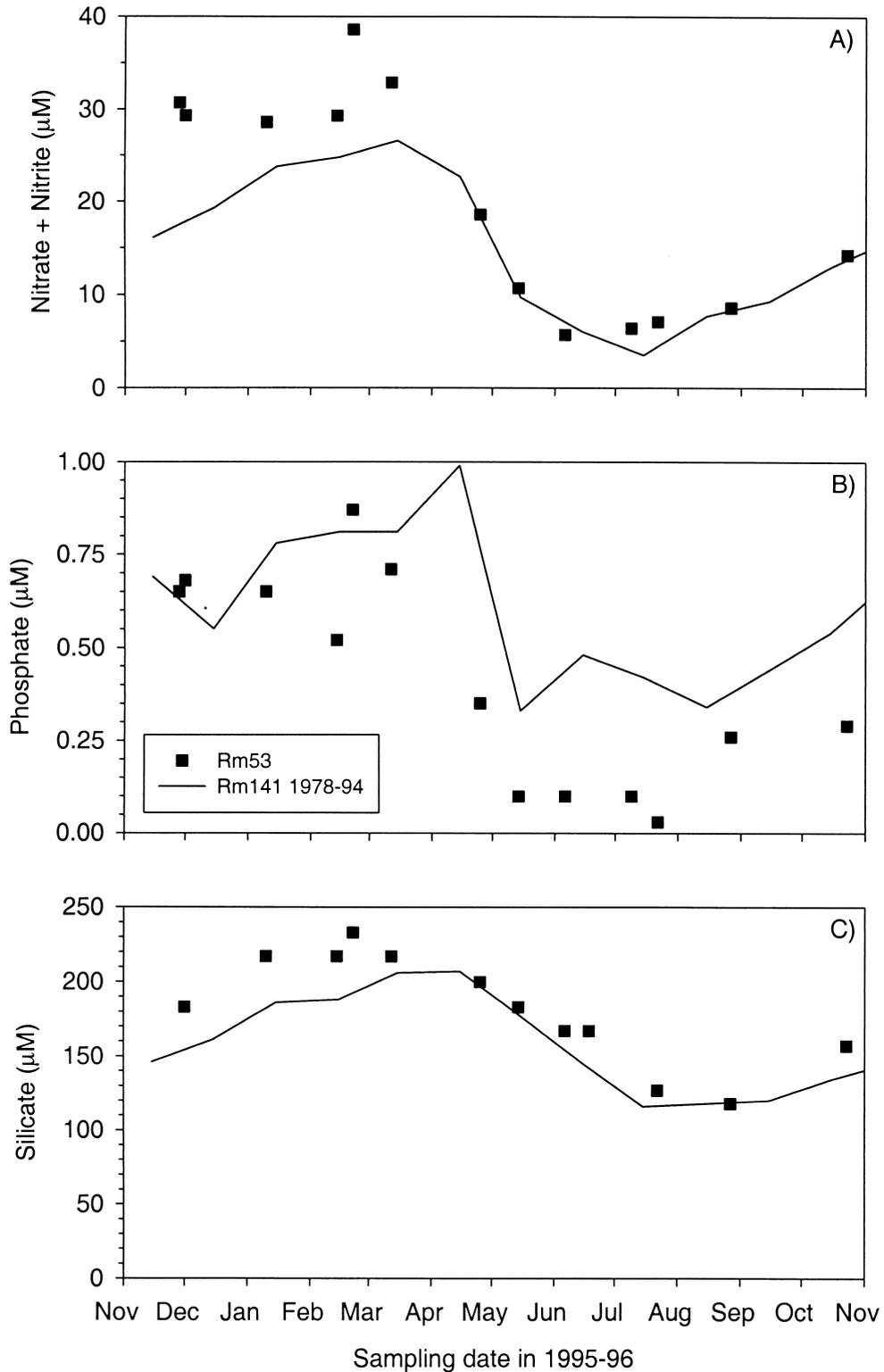


Fig. 9. Comparison of nutrient (nitrate, phosphate, silicate) concentrations measured at Rm53 over a period of 1 year in 1995–1996 (USGS data, unpublished) with monthly average measurements at Rm141 (Fig. 2) for the 16 year time period from 1978–1994 (USGS data, <http://www.wrwaters.usgs.gov/wqn96cd>). Despite the significant distance separating Rm53 and Rm141, prior studies indicate that nutrient concentrations measured downstream of Bonneville Dam at concurrent times show no significant spatial difference (e.g. Dahm et al., 1981; Prahel et al., 1998).

phate in this river system and therefore phytoplankton production is probably not nutrient limited.

Human influence on SPM concentration and chemical composition. Twenty-one major hydroelectric dams were constructed in the Columbia River–Snake River basin between 1933 and 1984 (Dietrich, 1995). Seventeen of these dams were added between 1957 and 1975. This development rapidly converted the Columbia River above the Bonneville Dam (Rm141) into a string of interconnected slackwater reservoirs (Harden, 1996). The one exception is a small stretch (~50 miles) of free-running water in the Hanford Reach, a region just above the Snake River confluence with the Columbia River. Although not much historical data exist to draw upon, two lines of evidence suggest that the addition of these dams, which modified the river's natural flow pattern dramatically, altered water quality characteristics and thereby helped to stimulate phytoplankton production in this river system.

First, water temperature in the Columbia River has increased ~1°C since the mid-1950s (Fig. 10A). A set of monthly mean water temperature measurements at Bonneville Dam extending from 1938–1966 gave first hint of this increase (Moore, 1968). Moore assigned the cause for the perceived warming primarily to stepped-up operations at the Hanford nuclear reservation and secondarily to the 12 “run-of-the-river” dams then in place on the Columbia River–Snake River system. The record at Bonneville Dam shows that elevated water temperature extends beyond 1966, however. The Hanford nuclear reservation cannot account for the persistence of warmer water as operations at this government facility were not continued at a high level beyond the mid-1960s. But, nine more major hydroelectric dams were added after 1966 to the Columbia River–Snake River system. On this basis, the observed warming might be attributed to hydrographic conditions created by the interconnected network of slackwater impoundments created behind dams.

Water temperature in the Columbia River varies widely on a seasonal basis, a phenomenon evident prior to the addition of dams. Minimum values of ~4–5°C occur in winter, while maximum values of ~20°C occur in summer (August). Given this naturally large seasonal variation, climatic factors could potentially also play a hand in the apparent ~1°C warming. Notably, historical records for river flow show the “spring freshet” in the Columbia has decreased significantly since the mid-1940s. However, mean annual flow, and particularly mean flow during August, the month of consistently warmest water temperature in any year, has remained approximately constant. Consequently, the recent decrease in peak flow during the “spring freshet” would not appear climate related. More likely, it is tied to water management practices made possible through completion in the mid-1960s to early 1970s of the extensive dam network on the Columbia River. Since the volume of water stored in the drainage basin has increased greatly as a consequence of large impoundments behind dams and mean river flow has remained approximately the same, the residence time of water within the drainage basin necessarily must have increased. Increased retention time of water would seem to be the primary cause for the noted small, but significant (~1°C) warming of the river since the mid-1950s.

The second line of evidence suggesting the addition of dams on the Columbia River has stimulated phytoplankton growth

relies on significant changes in SPM concentration. SPM concentration in the pre-dam Snake River and lower Columbia River was ~50 mg/L (van Winkle, 1914). This value is greater by perhaps a factor of 2 than what is observed today (Table 2). Addition of dams to the lower Columbia River (i.e., Bonneville, 1938; The Dalles, 1960; McNary, 1967; John Day, 1971) downstream of the confluence with the Snake River and within the Snake River itself (Ice Harbor, 1962; Lower Monument and Little Goose, 1970; Lower Granite, 1975) may explain this reduction in sediment load. The Snake River is recognized as a dominant source of SPM to the lower Columbia River (Whetten et al., 1969). The latter four dams have specifically changed the natural hydraulic connection of the Snake River with the mainstem Columbia River and all eight have impacted the capacity of this river system to transport sediment downstream (Beasley et al., 1986). Reduced water flow in the large impoundments behind dams has allowed particles to settle and deposit, thereby decreasing the suspended load of the river.

The combined consequences of reduced flow velocity (i.e., increased water retention time and clarity and decreased vertical mixing intensity) would make river conditions more conducive for phytoplankton growth. The result would be “greening” of organic matter associated with SPM transported downstream by the Columbia River to its estuary, beyond what prevailed under the natural, pre-dam flow conditions.

Biogeochemical effects of dams on other river systems. Rosenberg et al. (1997) assembled a literature review which suggests the addition of major dams to rivers has environmental consequences that are not as benign as once thought. Potential deleterious impacts include enhanced bioaccumulation of metals (e.g., methyl mercury) within foodwebs established in impoundments behind dams, greenhouse gas emissions from such impoundments and shifts in riverine biodiversity both above and below dams. Our purported “greening” of SPM in the lower Columbia represents a specific example of this third type of impact, an example that is not without precedent.

In 1967, High Dam was constructed on the Nile River. Impeded river flow in the impoundment created by that dam led to a dramatic change in downstream suspended sediment transport. SPM concentrations, which displayed a very large seasonal range prior to damming (30 to 3000 mg/L) with peak values evident during the flood season, assumed a more constant level year round (15 to 40 mg/L; White, 1988). The shift in water clarity was accompanied by an increase in algal production, a presumed cause—effect response. In 1971, Iron Gate dam was constructed on the Danube River. Time series data shows mean winter time dissolved silicate concentrations declined downstream soon after completion of that dam, a response attributed to diatom production and biogenic silica deposition within the impoundment created behind that dam (Humborg et al., 1997). In 1959, a system of canals, dams and locks was added to the Saint Lawrence River. This development completed the Saint Lawrence Seaway, a 3769 km long international waterway linking the Great Lakes with the Gulf of Saint Lawrence. Resultant slackwater in the Saint Lawrence River displays SPM biogeochemistry like that documented by our study of the post-dam Columbia. Chemical characterization of Saint Lawrence River SPM shows that POC contribution derives predominantly from autochthonous production in summer, and from terrestrial sources at other times (Pocklington

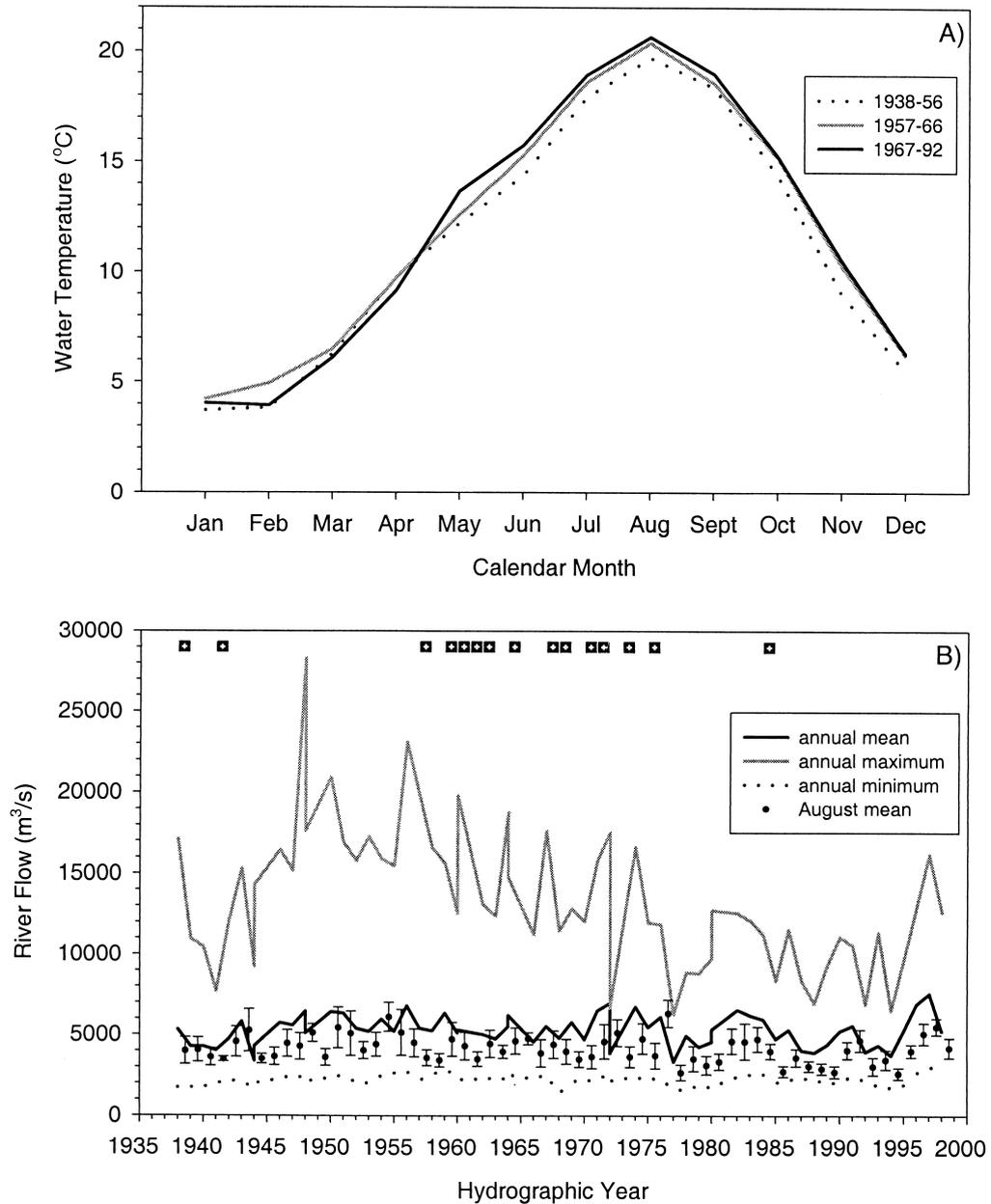


Fig. 10. Historical record for (A) monthly averaged water temperature at Bonneville Dam (Moore, 1968 and USGS data, unpublished) and (B) river flow (mean annual, minimum, maximum and August mean) at The Dalles (<http://waterdata.usgs.gov>) for the period of time from 1938 to 1992. Symbols with plus signs in the bottom graph indicate times when major hydroelectric dams were added to the Columbia River–Snake River system. The date of construction and power-generating capacity of the 21 major hydroelectric dams now present (Dietrich, 1995) are 1933, Rock Island (622 MW); 1938, Bonneville (1050 MW); 1941, Grand Coulee (6180 MW); 1957, McNary (980 MW); 1959, Brownlee (675 MW); 1960, The Dalles (1780 MW); 1961, Priest Rapids (789 MW), Rocky Reach (1213 MW), Chief Joseph (2069 MW), Oxbow (220 MW); 1962, Ice Harbor (603 MW); 1964, Wanapum (831 MW); 1967, Wells (774 MW), Hells Canyon (450 MW); 1968, Kennelside (flood control only); 1970, Lower Monument (810 MW), Little Goose (810 MW); 1971, John Day (2160 MW); 1973, Mica (1736 MW); 1975, Lower Granite (810 MW); 1984, Revelstoke (1843 MW).

and Tan, 1987). In years when discharge is greater than average, the proportion of terrigenous organic matter in POC is greatest. Unfortunately, there are no published data available to determine whether or not this seasonal trend was characteristic of SPM transported downstream in the Saint Lawrence River prior to damming.

Rivers which are naturally not very turbid, like the Columbia, may be poised at a threshold where a modest change in water flow conditions and a concomitant change in sediment transport capacity facilitates a dramatic shift in POC quality from dominance of allochthonous contribution to dominance of autochthonous phytoplankton production. On the other hand,

ivers like the Mississippi, viewed by some authorities (e.g., Mark Twain) as “too thick to drink, too thin to plow,” or like the Yangtze, may be biogeochemically insensitive to such dramatic hydrologic changes in response to damming because of their intrinsic flow character and naturally high turbidity. Although impeded flow in the impoundments behind dams in these turbid river systems would also act to reduce SPM concentrations, waters may still remain too turbid and vertically well-mixed to allow significant autochthonous production.

5. CONCLUSIONS

Beginning in early spring, significant diatom production appears annually in waters of the lower Columbia River. Comparison with data obtained between 1990–1999 as part of an LMER project (Table 2; Small and Morgan, 1994; Prahel et al., 1997) indicates the pattern for diatom production documented in the lower Columbia is not unique to our 1 year study period. It is an annual, spring time phenomenon in this river. The degree of diatom production appears broadly tied to river flow, being greater in years when spring time discharge is lower. This seasonal pattern in production, its apparent inverse correlation with river flow, and generally abundant levels of all nutrients year round suggest that diatom production in the lower Columbia River today is limited by water retention time in the system and by light availability controlled by vertical mixing dynamics and turbidity derived predominately from suspended detrital minerals. Interannual variance of these physical conditions governs the degree of interannual variability in riverborne phytoplankton production.

Historical records indicate that SPM concentrations in the Columbia River were never very high, but have dropped by a factor of 2 or more from values of ~50 mg/L in pre-dam days to ~20 mg/L or less today. Construction of 21 major dams in the Columbia River–Snake River drainage since the 1930s has created a network of interconnected pools where suspended particles apparently settle and deposit due to slackened water flow. Such particle loss and slackened flow should increase the overall water-column stability and allow greater light penetration into the water column, thus stimulating phytoplankton growth in the river. Given that this scenario applies to the Columbia River as it exists today, phytoplankton in the past may have contributed less to suspended organic matter in the Columbia River and other fluvial systems whose hydrographs have been highly modified by damming [e.g., Danube (Humborg et al., 1997); Nile (White, 1988); St. Lawrence (Pocklington and Tan, 1987)].

If major dams in the Columbia drainage, particularly those on the lower Snake River, were removed, one might predict a significant decrease in organic carbon input to the estuary from riverborne phytoplankton production. This change would be in response to an increase in river flow and SPM concentration, and consequently a decrease in water retention time and light availability for phytoplankton production. The prospect that primary production in a large river like the Columbia is sensitive to such water flow management practices requires further study. This point is particularly relevant to the Columbia River drainage where intense debate now rages about whether or not a strategic set of major dams should be removed to facilitate recovery of native salmon runs in the Pacific Northwest.

Such dam removal could have downstream ecological consequences. Turbidity maxima (ETM) in the Columbia estuary now inherit riverborne SPM enriched in organic matter that is derived from freshwater diatoms (Small and Morgan, 1994; Prahel et al., 1997). One might extrapolate from our yet limited dataset that freshwater diatom contribution to organic matter concentrated in ETM was significantly less prior to extensive damming of the Columbia River. If so, was the ETM then a more, or less, important site for biological transformation at the land–sea interface (Crump et al., 1997) than it is today? Significant shifts in the quantity and, in particular, quality of organic matter exported by the river to its estuary tied to major watershed management decisions (Hobbie, 2000) could have profound effects on trophodynamics in the Columbia estuary. These effects need to be clearly identified and carefully taken into consideration as general models for the ecological function of ETM in the Columbia River and other large river systems are developed and water management decisions are made.

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