*Wat. Res.* Vol. 28, No. 2, pp. 453–464, 1994
Printed in Great Britain. 

0043-1354/94 $6.00 + 0.00


# NUTRIENT DYNAMICS IN RIVERBEDS: THE IMPACT OF SEWAGE EFFLUENT AND AQUATIC MACROPHYTES

P. A. CHAMBERS[1] and E. E. PREPAS[2]

[1]National Hydrology Research Institute, 11 Innovation Blvd, Saskatoon, SK S7N 3H5 and [2]Zoology Department and Meanook Biological Station, University of Alberta, Edmonton, AB T6G 2E9, Canada

*(First received November 1992; accepted in revised form April 1993)*

**Abstract**—To determine the impact of nutrient loading from a sewage treatment plant and from aquatic macrophytes on riverbed chemistry, a 6-month (May–November) study was undertaken in the South Saskatchewan River, Saskatchewan, Canada at five sites located upstream and downstream of a municipal sewage treatment plant outfall and with differing biomasses of aquatic macrophytes. Nitrogen and phosphorus concentrations in the sediment-bound and porewater pools of the riverbed were greatest and porewater dissolved oxygen concentrations were lowest at the site with highest open-water nutrient concentrations (118 and 553 $\mu$g/l TP and TDN) and aquatic macrophyte biomass (205 g/m$^2$). Sites receiving little or no sewage effluent (23–60 $\mu$g/l TP and 221–325 $\mu$g/l TDN) had the lowest porewater and sediment-bound nutrient concentrations if no macrophytes were present, whereas concentrations were one-third to seven-fold greater if macrophytes were present in moderate abundance (135 g/m$^2$). Our results showed that effluent loading and aquatic macrophytes may cause significant changes in the chemistry of riverbed sediments and suggest that for shallow slow-flowing rivers, benthic nutrient exchanges represent a critical component in water quality modeling.

*Key words*—rivers, sediments, nutrients, aquatic macrophytes, phosphorus, nitrogen

## INTRODUCTION

The impact of increased nutrient loading on lentic ecosystems has been well documented, particularly with respect to changes in water and sediment chemistry and phytoplankton production (e.g. Schindler, 1974; Edmondson and Lehman, 1981). These findings have been incorporated into water quality models to predict the impacts of nutrient loading on open-water nutrient concentrations, primary production and higher trophic levels in lakes (Dillon and Rigler, 1975; Di Toro *et al.*, 1983; Câmara and Randall, 1984). In contrast, much less is known about eutrophication in river ecosystems, particularly the impact of added nutrients on riverbed sediments and benthic biota, and exchanges between the open water and the riverbed. Observed enhancements of primary and secondary production by nutrient loading (Chambers *et al.*, 1989; Johnston *et al.*, 1990; Bothwell, 1992) indicate that nutrient additions to rivers cause changes that extend beyond the direct effects on water chemistry. The findings that riverbed sediments can act as a buffer system in the control of soluble reactive phosphorus concentrations in surface water (Gessner, 1960; Taylor and Kunishi, 1971; Meyer, 1979; Klotz, 1988) and that benthic vegetation can trap suspended particulates (Gregg and Rose, 1982), take up nutrients from the sediments (Chambers *et al.*, 1989) and release them to the water column (Peverly, 1985) indicate the importance of riverbed sediments and biota in nutrient cycling. However, despite indications that riverbed processes can modify instream nutrients, the standard water quality models for predicting downstream dissipation of point-source nutrient loads are primarily hydraulic and focus on advection or advection–diffusion kinetics. Knowledge of the role of riverbed nutrient dynamics is critical for the development of realistic water quality models, particularly for shallow, low-nutrient and/or slow-flowing rivers where the potential for exchange of nutrients between open-water and riverbed pools is considerable. Moreover, the potential for benthic plants to modify riverbed sediments may mitigate management programs aimed at rooted plant control through reduced open-water nutrient loading.

The aim of this study was to characterize the nutrient pool in the riverbed of a regulated river in western Canada and to assess the effect of increased open-water nutrient loading and benthic primary production on riverbed chemistry. Many rivers in western Canada receive sewage inputs from sewage lagoons or municipal sewage treatment plants. In the broad (75–300 m), shallow (< 3 m deep) rivers of the Canadian prairies, these nutrient-enriched reaches are dominated by rooted aquatic plants which can achieve biomasses > 1000 g/m$^2$. This work forms part of a larger study aimed at modelling the role of benthic processes in river systems and establishing nutrient loading criteria to improve water quality and reduce excessive aquatic macrophyte growth in prairie rivers. A 6-month (May–November) study of

nutrient pools in the South Saskatchewan River, Saskatchewan was undertaken whereby open-water, porewater and sediment-bound (total and exchangeable) phosphorus and nitrogen concentrations were monitored at five sites located upstream and downstream of a municipal sewage treatment plant outfall and with various biomasses of aquatic macrophytes. This allowed us to test the hypotheses that: (1) sewage loading to a regulated river is associated with an increase in nutrient concentrations in the riverbed and (2) aquatic macrophytes can affect riverbed chemistry independent of any effects due to effluent loading.

## METHODS

*Study site*

The South Saskatchewan River is a seventh-order river and a major tributary of the Saskatchewan–Nelson river system. It originates in south-eastern Alberta, Canada with the convergence of the Bow and Oldman rivers and flows northeast across the prairies, joining with the North Saskatchewan River in east-central Saskatchewan to form the Saskatchewan River (Fig. 1). The latter flows through Cedar Lake and Lake Winnipeg into the Nelson River which drains into Hudson Bay. With the exception of the montane headwaters, the drainage basin is located entirely within the prairie ecozone of Canada which is characterized by a semi-arid climate, brown or black chernozemic soils, and vegetation dominated by short or mixed grass communities in the southern and central portions and trembling aspen and poplar to the north (Environment Canada, 1986).

Flows in the South Saskatchewan River are regulated by more than 20 dams in Alberta and the Gardiner Dam located 114 km upstream of the City of Saskatoon. Since completion of the Gardiner Dam in 1965, mean annual flows at Saskatoon have averaged 213 $m^3/s$ (1965–1986) with peak flows typically occurring in winter and minimum flows recorded during summer. Exceptions to this pattern occur when unusually high mountain snowpack in combination with heavy rainfall produces high flows in mid-summer. Operating guidelines for the Gardiner Dam require that a minimum flow of 42.5 $m^3/s$ be maintained in the river at Saskatoon throughout the year. In 1971, the City of Saskatoon (population 125,089) initiated primary sewage treatment. Effluent is discharged from the sewage treatment plant (STP) into the river through a series of diffusers originating 50 m off the west riverbank and extending one-third of the channel width (total width 300 m). Chlorination to kill bacteria was added in 1985 and in 1989 (the study year), the City (population 183,897) continued with

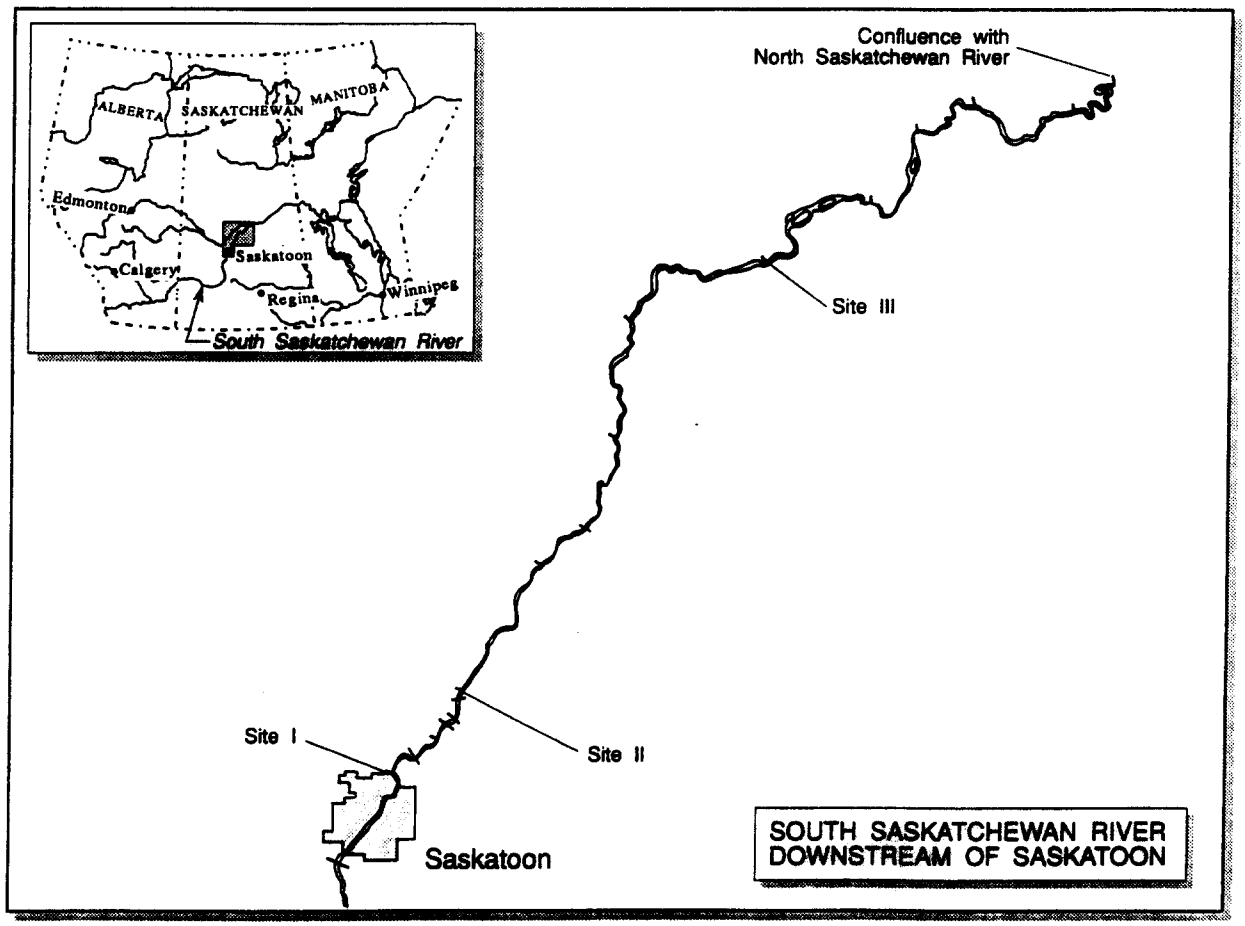


Fig. 1. Map of the Canadian prairie provinces showing the South Saskatchewan River and the study sites.

primary treatment and chlorination. Based on a 1980 study, 86% of the phosphorus load in the South Saskatchewan River at Saskatoon was derived from Gardiner Dam discharge (Tones *et al.*, 1980). Downstream of Saskatoon, approx. 86% of the phosphorus load was derived from the STP (May–Sept. 1988; Chambers, unpublished data).

Five study sites were selected on the basis of open-water quality and aquatic macrophyte biomass from data collected from 1987 and 1988 surveys of the river (Chambers *et al.*, 1989; Chambers, unpublished data) (Fig. 1). Site I was located approx. 100 m upstream of the Saskatoon STP outfall; aquatic macrophytes were absent, total phosphorus (TP) and total dissolved nitrogen (TDN) concentrations averaged 18 and 293 $\mu$g/l, respectively ($n = 21$ and 18; June–September 1987 and 1988). Site II was located 25 km downstream of the STP outfall. Here, the plume of sewage effluent (discharged along the west bank of the river) had not completely mixed across the entire river. As a result, open-water nutrient concentrations were considerably less along the east riverbank [30 and 323 $\mu$g/l TP and TDN, respectively, ($n = 8$ and 6); June–September 1987 only] than along the west bank [113 and 571 $\mu$g/l TP and TDN, respectively ($n = 21$ and 19); June–September 1987 and 1988]. In addition, aquatic macrophyte biomass peaked at $205 \pm 72$ g/m$^2$ dry weight (August 1988; mean $\pm$ SE) along the west riverbank while rooted plants were absent along the east bank. Sampling stations were established along both the west and east riverbanks and henceforth will be referred to as Site II-weed and Site II-nonweed, respectively. Site III was located 150 km downstream of the STP outfall. Here, the effluent plume was mixed across the entire width of the river and TP and TDN concentrations averaged 38 and 271 $\mu$g/l, respectively ($n = 13$; June–September 1988 only). Aquatic macrophytes were confined to an area extending approx. 55 m off both shores with peak biomasses of $135 \pm 19$ g/m$^2$ dry weight (August 1988). Two sampling stations were established: Site III-weed located approx. 45 m offshore of the west bank and Site III-nonweed located approx. 70 m offshore of the west riverbank.

*Sampling methods*

The five stations were visited on 35 occasions between May and November 1989. On each date, open-water samples were collected 15–30 cm below the water surface for phosphorus [total (TP), total dissolved (TDP) and soluble reactive (SRP) phosphorus] and nitrogen [total dissolved (TDN), nitrate + nitrite ($NO_2 + NO_3$) and ammonium ($NH_4$)] analyses. Flow-weighted sewage effluent samples were collected daily between May and August 1989 and analyzed for TP, TDP, SRP, TDN, $NO_2 + NO_3$ and $NH_4$. Samples for TDN, TDP and SRP were filtered in the field through pre-washed 0.45-$\mu$m Sartorius membrane filters; samples for $NH_4$ analysis were preserved with 0.25-ml 40% v/v $H_2SO_4$. All samples were stored on ice in coolers and then refrigerated at 4°C in the laboratory until analyzed. Current velocity was measured at each station with a Gurly–Price model 22 current meter at 0.1 and 0.25 m below the water surface and 0.1 m above the riverbed. Mean current velocity was calculated as the average of the three readings.

Porewater and sediment samples, and open-water Ca and DO samples were collected on 7–10 sampling dates for each station. Porewater was sampled with 80-ml single chamber dialyzers ("gravel peepers"; Sly, 1988) fitted with biologically inert membranes (Gelman HT-450). The samplers were filled with degassed distilled deionized water and allowed to equilibrate in a closed water bath bubbled with nitrogen gas for at least 4 days prior to use. Two racks, each containing three peepers stacked vertically, were inserted side-by-side into the riverbed at each station, ensuring that the same location (within 1–2 m$^2$) was maintained throughout the entire study. As each sampler measured 6 cm dia., porewater samples were integrated over three depth intervals: 0–6, 6–12 and 12–18 cm into the riverbed. The samplers were allowed to equilibrate with the pore water for a minimum of 2 weeks before retrieval (Sly, 1988). On each sampling date, two racks (i.e. six samplers) were retrieved from each station. Pore water was recovered from the samplers with syringes. Samples for SRP, $NH_4$, Ca and $Fe^{2+}$ analysis were injected into glass vials that had been gassed with nitrogen and capped with Wheaton stoppers. Samples for dissolved oxygen (DO) analysis were fixed in the syringe following the micro-Winkler method of Burke (1962). All porewater samples were removed from the sampler within 5 min of retrieval to reduce contact with the air and chemical precipitation. The samples were kept in the dark on ice until analyzed. Two sediment cores (20 cm long, 5 cm i.d.) were collected at each station within 2 days of porewater collection. The cores were extruded and sectioned into 6-cm slices that were frozen for subsequent analysis.

*Analytical methods*

Surface water samples were analyzed for TP, TDP, SRP, TDN, $NO_2 + NO_3$ and $NH_4$ at the Western Regional Water Quality Branch Laboratory, Environment Canada following Environment Canada (1979). Samples for TP and TDP analyses were digested with potassium persulfate and sulfuric acid; TP, TDP and SRP were analyzed on a Technicon autoanalyzer following the molybdenum blue method. $NH_4$ and $NO_2 + NO_3$ were determined on a Technicon autoanalyzer; the $NH_4$ method was modified to use sodium salicylate, instead of phenol, as the reaction agent with sodium hypochlorite. TDN was analyzed by u.v. digestion followed by colorimetry on a Technicon autoanalyzer.

Porewater samples were analyzed for SRP, $NH_4$, $Fe^{2+}$, Ca and DO. All porewater samples were analyzed within 24 h of collection. SRP and $NH_4$ were analyzed on a spectrophotometer following the molybdenum blue method of Murphy and Riley (1962) and the phenol hypochlorite method of Solorzano (1969), respectively. $Fe^{2+}$ was analyzed on a spectrophotometer following the phenanthroline method (APHA *et al.*, 1985). Porewater and open-water DO was determined by titration against sodium thiosulfate following the Burke (1962) micro-Winkler method. Porewater and open-water Ca was analyzed by flame emission on a Perkin–Elmer (model 3030) atomic absorption flame emission spectrophotometer (APHA *et al.*, 1985). All porewater samples were analyzed in duplicate.

Sediment samples were analyzed for total and exchangeable nitrogen (N) and phosphorus (P). Total N and P were analyzed at the Freshwater Institute Laboratories, Fisheries and Oceans Canada, Winnipeg, Manitoba on dried sediments ground to pass through 100-$\mu$m mesh. Total phosphorus was extracted with 0.165 N HCl from ashed (1 h at 550°C) samples and analyzed on an autoanalyzer (after Stainton *et al.*, 1977). Total N was determined on a Control Equipment Model 24XA C-H-N analyzer. Exchangeable N and P were analyzed on previously-frozen sediments that were thawed to room temperature. Exchangeable P was extracted by shaking sediment samples for 16 h with 0.1 N NaOH–0.1 N NaCl (after Williams *et al.*, 1967) and measured spectrophotometrically (Murphy and Riley 1962). Exchangeable N was extracted by shaking sediment samples for 1 h with 2 M KCl (Bremner, 1965) and measured spectrophotometrically as ammonium (Solorzano, 1969). Exchangeable nutrient concentrations were expressed per dry weight of sediment as determined by drying wet sediments to constant weight at 110°C. Total nutrient analyses were performed in duplicate; exchangeable nutrient analyses were performed in triplicate.

*Statistical methods*

Data were analyzed with the Statistical Analysis System (SAS Institute Inc., 1988). Differences in open-water nutrient chemistry between sites was determined by multivariate analysis of variance (MANOVA). Comparisons of

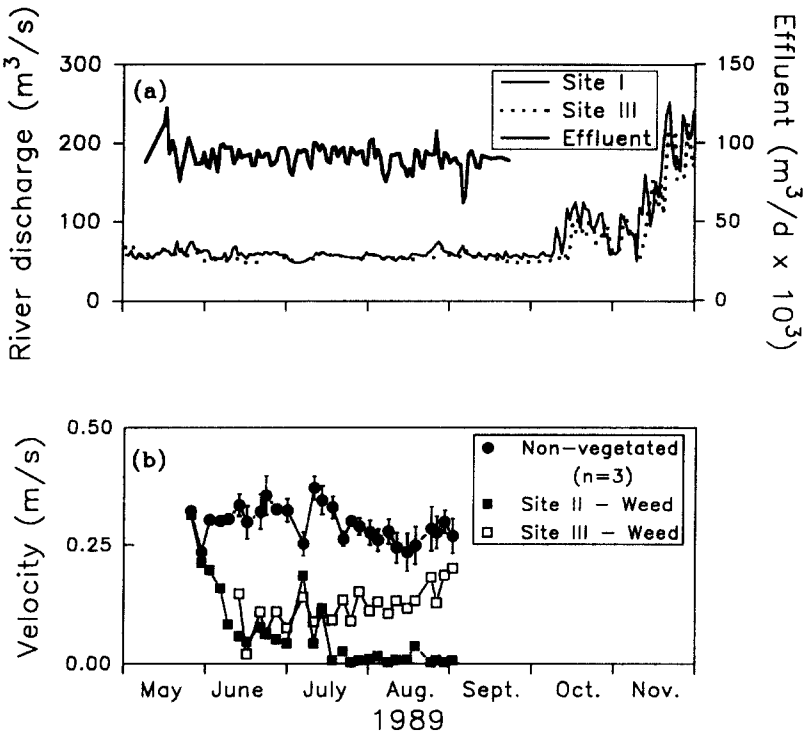


Fig. 2. Discharge rates and current velocities (mean of three depths) for the South Saskatchewan River, Saskatchewan: (a) discharge rate at Saskatoon (6.8 km upstream of Site I) and St Louis (Site III) (Environment Canada, 1990) and for the effluent from the Saskatoon STP and (b) current velocities for nonvegetated sites (mean of Sites I, II-nonweed and III-nonweed), Site II-weed and Site III-weed.

porewater and sediment chemistry between sites and depth strata were analyzed by MANOVA. There were no significant differences ($P > 0.05$) in porewater or sediment nutrient concentrations for samples collected from peepers or cores positioned side-by-side in the riverbed; the samples were therefore treated as duplicates. All ANOVA and MANOVA tests were followed by Student–Newman–Keuls (SNK) multiple range tests to identify differences in open-water, porewater or sediment chemistry between sites, dates and, in the case of riverbed samples, depth strata. Regression analysis was used to relate porewater SRP and $NH_4$ concentrations to sediment phosphorus and nitrogen concentrations for each depth strata. Porewater SRP and $NH_4$ concentrations were also related to open-water nutrient concentrations and current velocity (integrated over the 2 weeks prior to sampling) with site introduced as a dummy variable in the regression. Results are presented as mean $\pm$ 1 SE in the text; mean values are plotted in the figures.

## RESULTS

### *Surface water*

Discharge rate remained relatively constant throughout May–September 1989, averaging $58 \pm 0.4$ m$^3$/s 6.8 km upstream of Site I and $55 \pm 0.4$ m$^3$/s at Site III (Fig. 2). By October, flows had begun to increase reaching values in excess of 200 m$^3$/s by mid-November as a result of increased releases over the Gardiner Dam. While differences in discharge between the two sites were small, flows were consistently less at the downstream site ($P < 0.001$; $t$-test) due to high rates of evaporation (700–800 mm mean annual lake pan evaporation) relative to precipitation (300–400 mm mean annual) (Fisheries and Environment Canada, 1978). Effluent release rates from the STP averaged $90{,}430 \pm 682$ m$^3$/d, May–September 1989 and represented <2% of river discharge.

While discharge rate was only marginally different between the sites, current speed differed between the five locations (Fig. 2). Mean current speed was not significantly different ($P > 0.1$; ANOVA) for the three sites without macrophytes and averaged $0.29 \pm 0.01$, $0.27 \pm 0.02$ and $0.31 \pm 0.01$ m/s at Site I, Site II-nonweed and Site III-nonweed, respectively. By comparison, mean current speeds at the vegetated sites were significantly less ($P < 0.01$; ANOVA), averaging $0.03 \pm 0.01$ and $0.12 \pm 0.01$ m/s at Site II-weed and Site III-weed, respectively.

Open-water nutrient concentrations also differed between sites. Phosphorus (TP, TDP and SRP) and TDN concentrations were consistently lowest upstream of the STP (Site I) and greatest 25 km downstream along the west riverbank (Site II-weed) (Table 1, Fig. 3). Concentrations were intermediate at Sites II-nonweed, III-nonweed and II-weed with no significant differences ($P > 0.1$) between the vegetated and non-vegetated locations at Site III. In contrast, $NH_4$ and $NO_2 + NO_3$ concentrations were lowest at the furthest downstream sites (Sites

Table 1. Nutrient concentrations in the open-water, porewater and bottom sediments of the South Saskatchewan River, Saskatchewan at five sites. Data are presented as mean ± SE averaged from June to November 1989. Porewater and sediment data are also averaged over a depth extending from 0 to 18 cm below the sediment–water interface

| | Nonweed | | | Weed | |
|---|---|---|---|---|---|
| | Site I | Site II | Site III | Site II | Site III |
| *Open-water (μg/l)* | | | | | |
| TP | 23 ± 7 | 48 ± 2 | 60 ± 3 | 118 ± 9 | 60 ± 3 |
| TDP | 8 ± 1 | 35 ± 2 | 49 ± 3 | 97 ± 9 | 49 ± 3 |
| SRP | 4 ± 0.3 | 21 ± 2 | 31 ± 3 | 72 ± 8 | 29 ± 3 |
| TDN | 221 ± 6 | 325 ± 12 | 259 ± 8 | 553 ± 24 | 277 ± 12 |
| $NH_4$ | 18 ± 2 | 61 ± 7 | 13 ± 1 | 158 ± 26 | 16 ± 1 |
| $NO_2 + NO_3$ | 45 ± 5 | 81 ± 10 | 13 ± 3 | 198 ± 14 | 10 ± 0.2 |
| *Porewater* | | | | | |
| SRP (μg/l) | 21 ± 4 | 36 ± 6 | 71 ± 8 | 627 ± 48 | 356 ± 18 |
| $NH_4$ (μg/l) | 347 ± 48 | 219 ± 37 | 141 ± 23 | 2372 ± 268 | 931 ± 55 |
| $Fe^{2+}$ (μg/l) | 193 ± 30 | 151 ± 26 | 171 ± 19 | 2511 ± 282 | 873 ± 142 |
| Ca (mg/l) | 33 ± 1 | 36 ± 2 | 30 ± 2 | 51 ± 3 | 27 ± 1 |
| DO (mg/l) | 2.4 ± 0.3 | 2.8 ± 0.4 | 1.8 ± 0.2 | 1.0 ± 0.1 | 1.4 ± 0.1 |
| *Bottom sediments (μg/g dw)* | | | | | |
| Exchangeable P | 87 ± 11 | 110 ± 6 | 105 ± 7 | 214 ± 12 | 152 ± 7 |
| Exchangeable N | 3.9 ± 0.9 | 3.4 ± 0.6 | 3.5 ± 0.7 | 29 ± 6 | 7.7 ± 1.4 |
| Total P | 378 ± 29 | 419 ± 21 | 331 ± 12 | 638 ± 17 | 440 ± 12 |
| Total N | 115 ± 22 | 126 ± 13 | 119 ± 25 | 436 ± 58 | 277 ± 29 |

III-weed and nonweed), greatest at Site II-weed and intermediate at Sites I and II-weed. Nutrient concentrations in the effluent averaged 4.1 ± 0.1 mg/l TP and 20.0 ± 0.2 mg/l TDN throughout the summer (May–September 1989).

Open-water nutrient concentrations were relatively constant throughout the year at the upstream site (Site I) (Fig. 3). By comparison, downstream concentrations varied considerably over the year generally in response to fluctuating discharge and nutrient concentrations of the effluent. However, a two to three-fold increase in TP, TDP and SRP concentrations was observed at the high biomass site (II-weed) from mid-July to mid-August despite relatively constant loads from the STP. This indicates an unidentified short-term source of nutrient loading in the 25 km reach below the STP such as from a spill or internal nutrient loading from the sediments to the

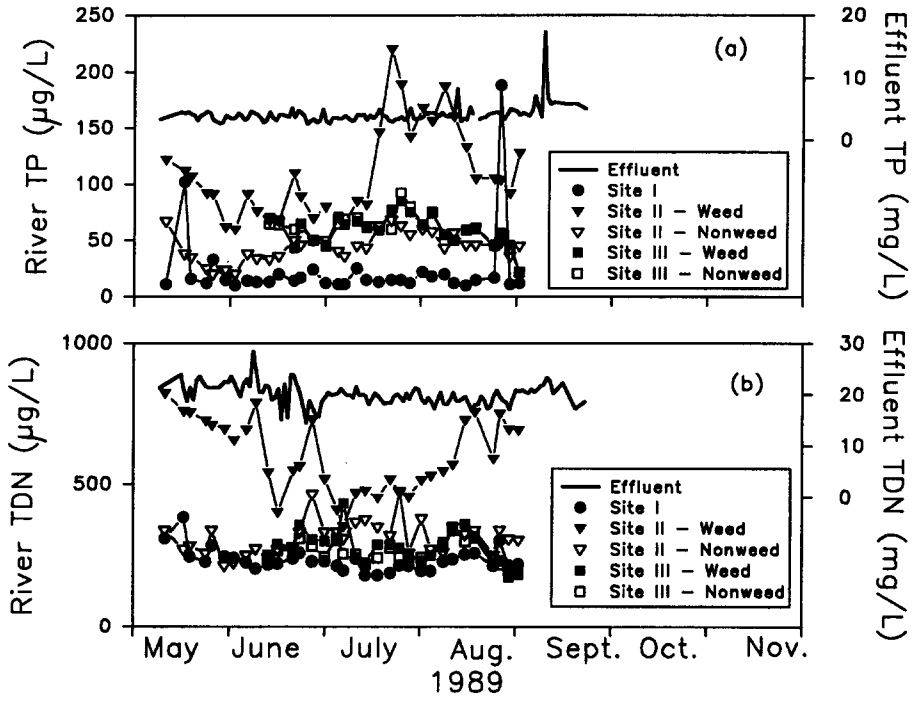


Fig. 3. Surface-water nutrient concentrations for five sites on the South Saskatchewan River, Saskatchewan and effluent concentrations for the Saskatoon sewage treatment plant: (a) total phosphorus (TP) concentrations and (b) total dissolved nitrogen (TDN) concentrations.

open-water. Dominant ion concentrations did not differ between sites or dates and averaged 42, 29, 2.9, 17, 87 and 9.4 mg/l Ca, Na, K, Mg, $SO_4$ and Cl, respectively.

*Porewater chemistry*

Porewater nutrient concentrations differed significantly between vegetated and nonvegetated sites (Table 1). Comparison of porewater SRP, $NH_4$ and $Fe^{2+}$ concentrations averaged over depth and date showed that sites without submerged plants did not differ significantly ($P > 0.1$) and were consistently less nutrient rich ($P < 0.05$) than sites with macrophytes. Moreover, for the two sites with macrophytes, porewater SRP, $NH_4$ and $Fe^{2+}$ concentrations were consistently greater for the site with higher biomasses of aquatic vegetation (Site II-weed). Differences in DO concentrations between sites were consistent with respect to nutrient chemistry and aquatic macrophyte abundance: DO concentrations were lowest at the high biomass nutrient-rich site, highest at the low-nutrient nonvegetated sites and intermediate at the site with moderate biomass and nutrient concentrations. Porewater Ca concentrations were greatest at the high biomass nutrient-rich site but showed no consistent pattern with changes in aquatic macrophyte abundance or nutrients for the other four sites.

In addition to differences between sites, porewater chemistry varied with depth and date (Fig. 4). There was, however, no consistent pattern in porewater temporal variation between sites with and without plants. Strong depth gradients were rarely established at any site. However despite this weak stratification, porewater DO concentrations were almost always less than open-water values and, with the exception of May and November samples, always less than 4 mg/l. Even at sites with coarse substrates (cobble at Site I and sand at Site II-nonweed), porewater DO values averaged less than 3 mg/l while at the high biomass site (Site II-weed), concentrations were $\leqslant 1$ mg/l for most of the summer. Porewater SRP and $NH_4$ concentrations also tended to be greater than open-water values for vegetated sites. However, at sites without macrophytes, open-water nutrient concentrations were often similar to porewater values, particularly for the shallowest depth strata. Ca concentrations were generally greater in the open-water than in the porewater except at the high biomass nutrient-rich site where they were indistinguishable.

Porewater SRP, $NH_4$, $Fe^{2+}$, DO and Ca concentrations were highly intercorrelated (Table 2). Analysis of porewater data for all sites and depths showed that SRP, $NH_4$ and $Fe^{2+}$ concentrations were all positively correlated with one another. SRP, $NH_4$ and $Fe^{2+}$ were negatively correlated with DO. While Ca was positively correlated with SRP, $NH_4$ and $Fe^{2+}$, removal of the high biomass nutrient-rich site from the data set (i.e. Site II-weed, the only site with significantly different porewater Ca concentrations) resulted in negative correlations with SRP ($r = -0.25$, $0.001 < P < 0.01$) and $NH_4$ ($r = -0.35$, $P \leqslant 0.0001$) and a positive correlation with DO ($r = 0.40$, $P \leqslant 0.0001$).

*Sediment chemistry*

Differences in sediment chemistry between sites were consistent with porewater chemistry (Table 1). Concentrations of both exchangeable and total phosphorus and nitrogen were greatest at the heavily-weeded site (Site II-weed), intermediate at the site with moderate macrophyte growth (Site III-weed) and lowest at the sites without macrophytes. While sediment nitrogen and phosphorus concentrations varied with depth and date, there were no consistent patterns and depth gradients were rarely established (Fig. 5). Changes in sediments nutrient concentrations were, however, highly intercorrelated (Table 2).

*Open-water, porewater and sediment inter-relations*

Nitrogen and phosphorus concentrations in the porewater and sediment-bound or open-water pools were highly correlated ($P < 0.005$, Table 2) when data from all sites were pooled. However, within each site, there were no correlations ($P > 0.1$) between nutrients in the porewater and open-water or sediment-bound pools. There was also no correlation between porewater nutrient concentrations and current velocity ($P > 0.26$) averaged over the 2 weeks prior to sampling for a depth of 0.1 or 0.25 m below the water surface, 0.1 m above the sediment–water interface or averaged for the entire water column.

## DISCUSSION

Nutrient concentrations in the bottom sediments of the South Saskatchewan River varied in response to open-water effluent loads and the presence/absence of aquatic macrophytes. Total, exchangeable and porewater phosphorus and nitrogen concentrations in the riverbed were greatest at the site with highest open-water nutrient concentrations (118 and 553 $\mu$g/l TP and TDN, respectively) and aquatic macrophyte biomass (205 g/m$^2$) and lowest at the sites with little or no effluent loading (23–60 $\mu$g/l TP and 221–325 $\mu$g/l TDN) and no aquatic macrophytes. Riverbed nutrient concentrations were intermediate at the site with little effluent loading (60 $\mu$g/l TP and 277 $\mu$g/l TDN) yet moderate aquatic macrophyte growth (135 g/m$^2$). Overall, porewater values ranged from below detection limits to 1.7, 2.4 and 2.5 mg/l SRP, $NH_4$ and $Fe^{2+}$ while sediment-bound concentrations ranged from $<1$ to 116 $\mu$g/g exchangeable nitrogen, 28 to 360 $\mu$g/g exchangeable phosphorus, 215 to 770 $\mu$g/g total phosphorus and 10 to 1550 $\mu$g/g total nitrogen. These concentrations are consistent with values previously reported for other streams and rivers (Dahm *et al.*, 1987; Carr, 1989; Chambers *et al.*, 1992) and are similar to concentrations found

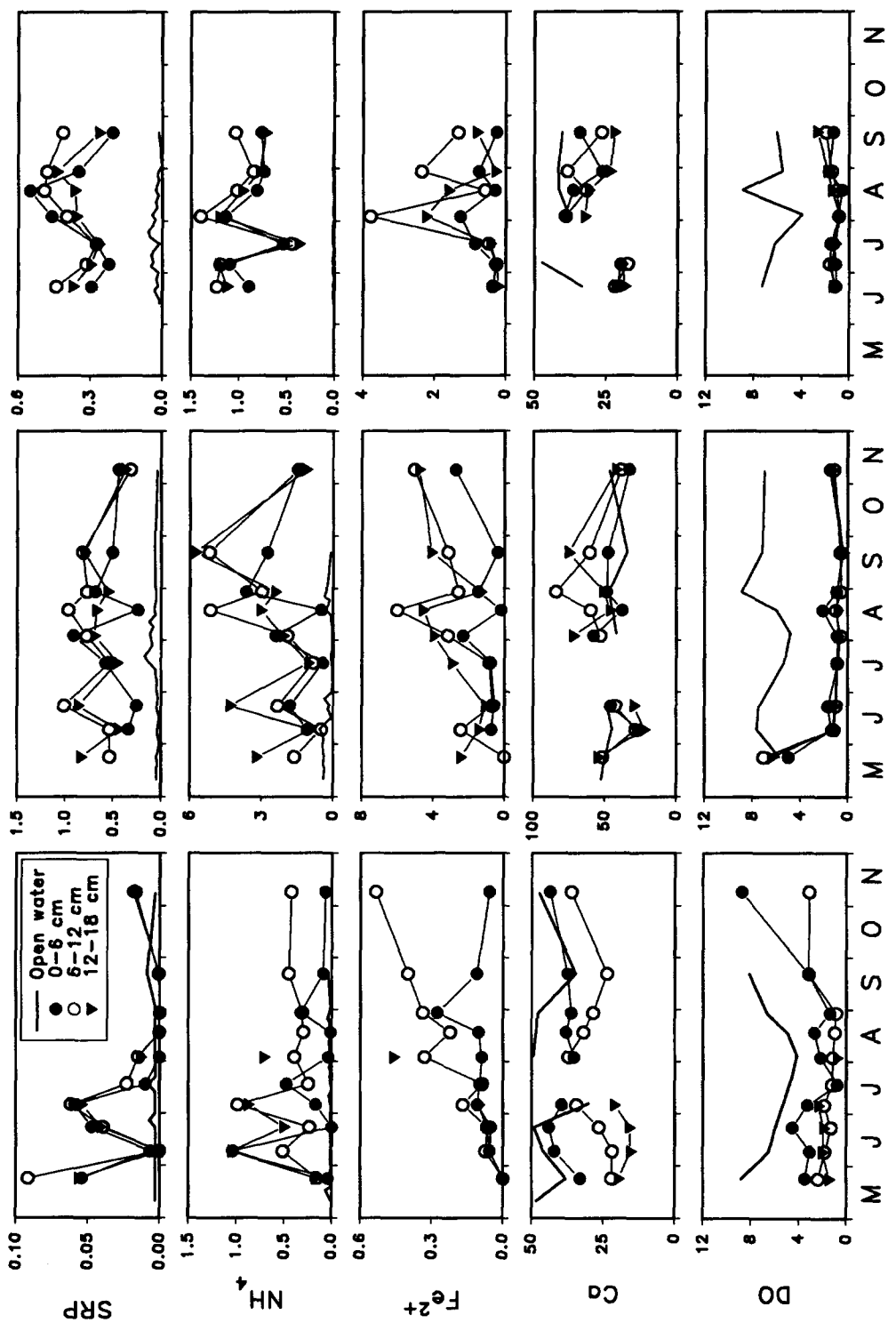


Fig. 4. Open-water and porewater SRP, $NH_4$, Ca and DO concentrations and porewater $Fe^{2+}$ concentrations at for Sites I, II-weed and III-weed on the South Saskatchewan River, Saskatchewan. Site I is presented as representative of the three sites without aquatic macrophytes. (Open-water concentrations are not always distinguishable from zero on these scales. Note changes in scale for SRP, $NH_4$, $Fe^{2+}$ and Ca between sites.)

Table 2. Correlation matrix for porewater soluble reactive phosphorus (SRP), ammonium ($NH_4$), ferrous iron ($Fe^{2+}$), calcium (Ca) and dissolved oxygen (DO) concentrations and sediment total and exchangeable phosphorus (P) and nitrogen (N) concentrations for all depth strata and all stations on the South Saskatchewan River, Saskatchewan. Data presented as Pearson correlation coefficients ($r$) and sample size

| | Porewater | | | | | Sediment | | | |
|---|---|---|---|---|---|---|---|---|---|
| | SRP | $NH_4$ | $Fe^{2+}$ | DO | Ca | Exch-P | Exch-N | Total P | Total N |
| *Porewater* | | | | | | | | | |
| SRP | 1.00 (182) | | | | | | | | |
| $NH_4$ | 0.84*** (182) | 1.00 (186) | | | | | | | |
| $Fe^{2+}$ | 0.64*** (182) | 0.65*** (183) | 1.00 (183) | | | | | | |
| DO | −0.40*** (182) | −0.35*** (184) | −0.29***s (183) | 1.00 (184) | | | | | |
| Ca | 0.45*** (154) | 0.48*** (155) | 0.53*** (155) | −0.02 (155) | 1.00 (155) | | | | |
| *Sediment* | | | | | | | | | |
| Exch-P | 0.65*** (77) | 0.53*** (77) | 0.55*** (77) | −0.32* (77) | 0.54*** (63) | 1.00 (91) | | | |
| Exch-N | 0.40** (77) | 0.42*** (77) | 0.13 (77) | −0.24 (77) | 0.38* (63) | 0.37** (91) | 1.00 (91) | | |
| Total P | 0.59*** (73) | 0.52*** (73) | 0.36* (73) | −0.36* (73) | 0.57*** (59) | 0.61*** (76) | 0.62*** (76) | 1.00 (76) | |
| Total N | 0.46*** (73) | 0.37* (73) | 0.16 (73) | −0.28 (73) | 0.27 (59) | 0.52*** (76) | 0.80*** (76) | 0.52*** (76) | 1.00 (76) |

*$P \leq 0.01$; **$P \leq 0.001$; ***$P \leq 0.0001$.

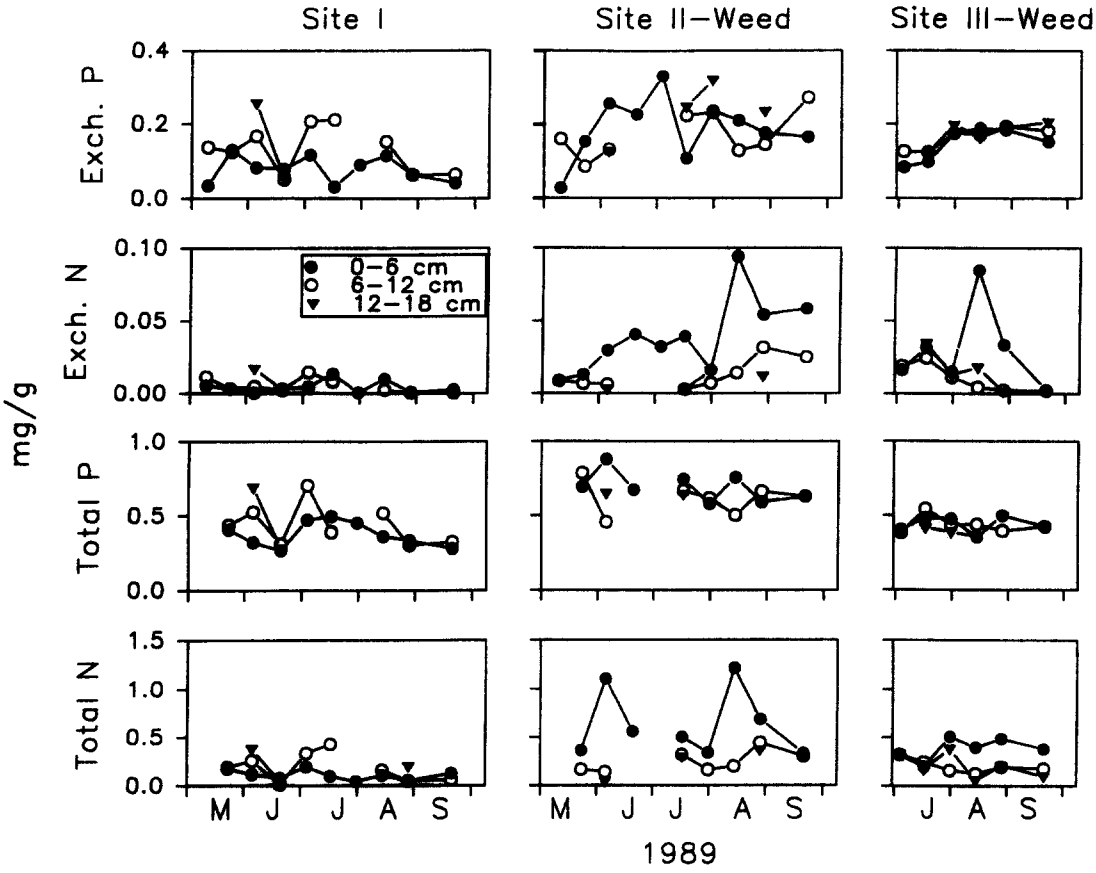


Fig. 5. Total and exchangeable phosphorus and nitrogen concentrations at three depth intervals into the riverbed for Sites I, II-weed and III-weed on the South Saskatchewan River, Saskatchewan. Site I is presented as representative of the three sites without aquatic macrophytes.

in mesotrophic to eutrophic lakes (Barko and Smart, 1980; Enell and Lofgren, 1988; Shaw and Prepas, 1990).

The direct effects of effluent loading on riverbed chemistry are difficult to isolate from the indirect effects caused by enhanced growth of aquatic macrophytes. Total, exchangeable and porewater nutrient concentrations did not differ significantly between nonvegetated sites that were unimpacted (i.e. upstream, 23 $\mu$g/l TP and 221 $\mu$g/l TDN) or only moderately impacted (i.e. Sites II-nonweed and III-nonweed, 48–60 $\mu$g/l TP and 259-325 $\mu$g/l TDN) by sewage effluent. Over this range, open-water nutrient concentrations had little effect on riverbed chemistry. Because of continuous plant cover at the heavily-impacted site (Site II-weed), the effects of aquatic macrophyte growth on riverbed chemistry could not be separated from those of open-water nutrient loading at this site. However, comparison of riverbed chemistry for vegetated and nonvegetated sites in a moderately-impacted reach showed that aquatic macrophytes had a significant impact on the chemistry of riverbed sediments. Thus, porewater nitrogen and phosphorus concentrations were 5–7-fold greater while sediment-bound nutrient concentrations were one-third to two times greater for the vegetated versus the nonvegetated site. In addition, porewater dissolved oxygen concentrations were lower while ferrous iron and ammonium concentrations were greater at the vegetated site.

The significance of aquatic macrophytes in altering sediment chemistry has previously only been reported for lakes. Here, macrophytes have been found to change sediment chemistry both passively, by trapping fine particulates and contributing organic matter during die-back (Butcher, 1933; Westlake, 1961; Ladle and Casey, 1971; Werner and Weise, 1982; Gregg and Rose, 1982) and actively, through the release of oxygen into the rhizosphere (Armstrong, 1967; Tessenow and Baynes, 1975, 1978; Sand-Jensen and Prahl, 1982; Sand-Jensen *et al.*, 1982; Sorrell and Dromgoole, 1987; Gunnison and Barko, 1989). The ability of plants to release oxygen through their roots suggests that vegetated sediments should have lower available iron, phosphorus and ammonium concentrations due to increased sediment redox. However, oxygen release sufficient to overcome the reducing capacity of most submerged sediments has only been observed for small isoetid macrophytes growing in oligotrophic lakes with oxidized sediments (Tessenow and Baynes, 1978; Reddy and Patrick, 1984, 1986; Jaynes and Carpenter, 1986). Our observation that riverbed nutrient concentrations were greater and dissolved oxygen concentrations were lower in vegetated than nonvegetated areas receiving anthropogenic nutrient loading is consistent with studies on the effect of aquatic macrophytes on sediment chemistry in mesotrophic and eutrophic lakes (Carignan, 1985). Moreover, comparison of riverbed chemistry for the two vegetated sites showed that porewater, exchangeable and total nutrient concentrations were greater and porewater DO values were lower at the high versus the low biomass site. This finding suggests that not only does the presence or absence of macrophytes affect sediment chemistry but that their impact varies with plant biomass.

Differences in riverbed chemistry between adjacent moderately-impacted vegetated and nonvegetated sites suggests that the presence of macrophytes was largely responsible for the increased nutrient concentrations rather than nutrient-enriched sediments serving as the stimulus for plant growth. Our finding that current velocities measured prior to the onset of plant growth (late May) did not differ between nonvegetated, moderately vegetated and high biomass sites (Fig. 2) while summer (July–August) velocities differed significantly between these habitats (0.28, 0.13 and 0.03 m/s, respectively) is consistent with this hypothesis and suggests that the macrophytes themselves were responsible for decreasing current speed due to their increasing biomass and, in turn, enhancing particulate deposition and sediment reducing conditions. Madsen and Adams (1989) likewise noted that *Potamogeton pectinatus* occurred in stream sections where velocities had been considerably higher in the months preceding growth while Gregg and Rose (1982) observed that the presence of aquatic macrophyte enhanced deposition over nonvegetated controls. The ability of aquatic macrophytes to alter both their flow and sediment environment suggests that, providing nutrient concentrations exceed the minimum needed to support plant growth and current speeds are conducive to plant establishment ($\leqslant$1 m/s; Chambers *et al.*, 1991), aquatic macrophytes will establish and flourish. Once beds have become established, plants in the center of the beds will continue to act as a particulate filter and depositional site while those on the fringes will serve as pioneers in expanding the bed.

Few studies have examined the impact of anthropogenic nutrient loading on riverbed sediments and among those which have, the response of bottom sediments to nutrient enrichment is varied. Smith *et al.* (1978) observed that anthropogenic nutrient loading to the Crnojevica River, a weed-choked river in Yugoslavia, was associated with an exponential decrease in open-water TP concentrations and a linear decrease in sediment inorganic phosphorus concentrations yet no significant change in sediment total or organic phosphorus concentrations. Similarly, Fox *et al.* (1989) reported that Fe-bound phosphorus decreased while Ca- and saloid-bound phosphorus increased over a distance of 16 km downstream of the Ashford STP on the Great Stour River, England. These results suggest that the impact of anthropogenic nutrient loading on riverbed chemistry varies with the phosphorus species and the binding efficiency of the bottom sediments. Tessenow (1974) showed that in oxic water, more phosphorus adsorbed onto iron when Fe–P molar ratios were

greater than 1.8; at molar ratios less than 1.8 some Fe–P sorption may occur. Comparison of porewater Fe–P molar ratios for our three nonvegetated sites showed that the capacity of iron to adsorb phosphorus varied, averaging $5.29 \pm 1.83$, $4.72 \pm 1.07$ and $1.37 \pm 0.27$ at Sites I, II-nonweed and III-nonweed, respectively. At the vegetated sites, porewater Fe–P molar ratios averaged $2.25 \pm 0.4$ and $2.08 \pm 0.68$ (II-weed and III-weed, respectively). These findings demonstrate that within a reach of 125 km, riverbed sediments varied in their efficiency at binding phosphorus and hence, their ability to mitigate added nutrients.

In addition to variations in riverbed chemistry between sites, porewater and sediment-bound nutrients also varied with date and depth although consistent patterns and strong depth gradients were rarely if ever established. This lack of clear temporal or depth patterns is particularly surprising for the vegetated sites in that lake and laboratory studies have shown that aquatic macrophytes can mobilize 0.3–21 mg/l P, 12–20 mg/l $NH_4$, approx. 50 $\mu$g/g exchangeable phosphorus and 110–150 $\mu$g/g exchangeable nitrogen (Barko and Smart, 1980; Carignan, 1985; Chen and Barko, 1988) and cause a significant decrease in sediment nutrient concentrations (Carignan, 1985; Smith and Adams 1986) over one summer. Our observations that changes in riverbed chemistry at any site were not correlated with changes in either velocity or open-water chemistry indicate that the lack of seasonal or depth patterns in riverbed chemistry at any site is not due to irrigation with surface water. Comparison of porewater Fe–P molar ratios for all dates and depths showed that the phosphorus-binding efficiency of the sediments varied considerably with ratios less than 1.8 for 41, 81, 65, 54 and 37% of the samples from Sites I, III-weed, III-nonweed, II-weed and II-nonweed, respectively. In addition to changes in phosphorus-binding efficiency, trapping and accumulation of fine particulates and associated nutrients within the macrophyte beds may have obscured any decrease in riverbed nutrients due to plant uptake. While variable inputs from groundwater may also have obscured temporal changes in porewater chemistry, measurements of deuterium concentrations in porewater samples collected on 20 September 1989 from Site II-nonweed and Site III gave no evidence of groundwater intrusion (R. J. Cornett and P. A. Chambers, unpublished data).

In summary, our results showed that effluent loading and aquatic macrophytes may cause significant changes in the chemistry of riverbed sediments. Riverbed nutrient concentrations were greater and dissolved oxygen concentrations were less beneath high-biomass ($\sim 200$ g/m$^2$) macrophyte beds in heavily-impacted surface waters (118 $\mu$g/l TP, 553 $\mu$g/l TDN) than beneath moderate-biomass ($\sim 135$ g/m$^2$) beds in slightly-impacted waters (60 $\mu$g/l TP, 277 $\mu$g/l TDN). Moreover, porewater and sediment-bound nitrogen and phosphorus concentrations were one-third to seven-fold greater for vegetated versus non-vegetated areas despite identical open-water chemistry. The enrichment of riverbed sediments as a result of both direct loading from the open water and the indirect effects of increased aquatic macrophyte growth pose particular problems for water quality modeling of rivers. Riverbed sediments can represent either a sink of nutrients, under depositional conditions, or a source, under conditions conducive to internal loading or under high flows which suspend the bottom sediments and irrigate the riverbed. Moreover, riverbed nutrient concentrations cannot be predicted from open-water nutrient loading, even within a given river or geologic region, due to modifications by the benthic plant community. The impact of riverbed sediments and aquatic macrophytes on water quality will be of particular significance in the broad shallow rivers in the semi-arid region of central Canada and elsewhere, as well as in smaller rivers and streams throughout temperate and tropical regions, where aquatic macrophytes can grow abundantly. The potential for long-term reductions in water flow as a result of river regulation or regional climate warming will likely further increase the distribution of aquatic macrophytes and associated nutrient-rich reducing sediments. Inclusion of riverbed processes in water quality models will be critical for modeling downstream changes in river water quality in shallow, low-nutrient and/or slow-flowing rivers where the potential for exchange of nutrients between open-water and riverbed pools is considerable.

*Acknowledgements*—We thank W. Prompoj for leading the field program, and G. Hutchinson, K. Gibson and E. Robinson for technical assistance. This research was supported by Environment Canada/Water Quality Branch, Saskatchewan Environment and Public Safety, the City of Saskatoon, a Donner Canadian Foundation grant to P.A.C. and E.E.P. and a Canadian International Development Agency (CIDA) scholarship to W. Prompoj.

## REFERENCES

APHA, AWWA and WPCF (1985) *Standard Methods for the Examination of Water and Wastewater*, 16th edition. American Public Health Association, American Water Works Association and Water Pollution Control Federation, Washington, D.C.

Armstrong W. (1967) The use of polarography in the assay of oxygen diffusing from roots in anaerobic media. *Physiol. Plant* **20**, 540–553.

Barko J. W. and Smart R. M. (1980) Mobilization of sediment phosphorus by submersed freshwater macrophytes. *Freshwat. Biol.* **10**, 229–238.

Bothwell M. L. (1992) Eutrophication of rivers by nutrients in treated kraft pulp mill effluent. *Wat. Pollut. Res. J. Can.* **27**, 77–102.

Bremner J. M. (1965) Inorganic forms of nitrogen. In *Methods of Soil Analysis* (Edited by Black C. A.), pp. 1179–1237. American Society of Agronomy, Madison, Wis.

Burke J. D. (1962) Determination of oxygen in water using a 10-ml syringe. *J. Mitchell Soc.* **78**, 145–147.

Butcher R. W. (1933) Studies on the ecology of rivers. I. On the distribution of macrophytic vegetation in the rivers of Britain. *J. Ecol.* **21**, 58–91.

Câmara A. S. and Randall C. W. (1984) The QUAL II Model. *J. envir. Engng* **110,** 993–996.

Carignan R. (1985) Nutrient dynamics in a littoral sediment colonized by the submersed macrophyte *Myriophyllum spicatum*. *Can. J. Fish. Aquat. Sci.* **42,** 1303–1311.

Carr D. L. (1989) Nutrient dynamics of stream and interstitial waters of three first-order streams in New Mexico. M.Sc. thesis, University of New Mexico, Albuquerque, N.M.

Chambers P. A., Prepas E. E. and Gibson K. (1992) Temporal and spatial dynamics in riverbed chemistry: the influence of flow and sediment composition. *Can. J. Fish. Aquat. Sci.* **49,** 2128–2140.

Chambers P. A., Prepas E. E., Bothwell M. L. and Hamilton H. R. (1989) Roots versus shoots in nutrient uptake by aquatic macrophytes in flowing waters. *Can. J. Fish. Aquat. Sci.* **46,** 435–439.

Chambers P. A., Prepas E. E., Hamilton H. R. and Bothwell M. L. (1991) Current velocity and its effect on the growth of aquatic macrophytes in slow-flowing rivers. *Ecol. Appl.* **1,** 249–257.

Chen R. L. and Barko J. W. (1988) Effects of freshwater macrophytes on sediment chemistry. *J. Freshwat. Ecol.* **4,** 279–289.

Dahm C. N., Trotter E. H. and Sedell J. R. (1987) Role of anaerobic zones and processes in stream ecosystem productivity. In *Chemical Quality of Water and the Hydrologic Cycle* (Edited by Averett R. C. and McKnight D. M.), pp. 156–178. Lewis, Chelsea, Mich.

Dillon P. J. and Rigler F. H. (1975) A simple method for predicting the capacity of a lake for development based on lake trophic status. *J. Fish. Res. Bd Can.* **31,** 1519–1531.

Di Toro D. M., Fitzpatrick J. J. and Thomann R. V. (1983) Documentation for water quality analysis simulation program (WASP) and model verification program (MVP). Envir. Res. Lab, ORD, US EPA, Duluth, Minn, U.S.A. EPA-600/3-81-044.

Edmondson W. T. and Lehman J. T. (1981) The effect of changes in the nutrient income on the condition of Lake Washington. *Limnol. Oceanogr.* **26,** 1–29.

Enell M. and Lofgren S. (1988) Phosphorus in interstitial water: methods and dynamics. *Hydrobiologia* **170,** 103–132.

Environment Canada (1979) *Analytical Methods Manual*, Vol. 1. Inland Water Directorate, Water Quality Branch, Ottawa, Ontario.

Environment Canada (1986) *Terrestrial Ecozones of Canada*. Ecological Land Classification No. 19, Supply and Services Canada, Ottawa, Ontario.

Environment Canada (1990) *Surface Water Data Saskatchewan 1989*. Supply and Services Canada, Ottawa, Ontario.

Fisheries and Environment Canada (1978) *Hydrologic Atlas of Canada*. Supply and Services Canada, Ottawa, Ontario.

Fox I., Malati M. A. and Perry R. (1989) The adsorption and release of phosphate from sediments of a river receiving sewage effluent. *Wat. Res.* **23,** 725–732.

Gessner F. (1960) Untersuchungen uber den Phosphathaushalt des Amazonas. *Int. Rev. ges. Hydrobiol.* **45,** 339–345.

Gregg W. W. and Rose F. L. (1982) The effects of aquatic macrophytes on the stream microenvironment. *Aquat. Bot.* **14,** 309–324.

Gunnison D. and Barko J. W. (1989) The rhizosphere ecology of submersed macrophytes. *Wat. Resour. Bull.* **25,** 193–201.

Jaynes M. L. and Carpenter S. R. (1986) Effects of vascular and nonvascular macrophytes on sediment redox and solute dynamics. *Ecology* **67,** 875–882.

Johnston N. R., Perrin C. J., Slaney P. A. and Ward B. R. (1990) Increased juvenile salmon growth by whole-river fertilization. *Can. J. Fish. Aquat. Sci.* **47,** 862–872.

Klotz R. L. (1988) Sediment control of soluble reactive phosphorus in Hoxie Gorge Creek, New York. *Can. J. Fish. Aquat. Sci.* **45,** 2026–2034.

Ladle M. and Casey H. (1971) Growth and nutrient relationships of *Ranunculus penicillatus* var. *calcareus* in a small chalk stream. In *Proceedings of the European Weed Research Council 3rd International Symposium on Aquatic Weeds*, pp. 53–63.

Madsen J. D. and Adams M. S. (1989) The distribution of submerged aquatic macrophyte biomass in a eutrophic stream, Badfish Creek: the effect of environment. *Hydrobiologia* **171,** 111–119.

Meyer J. L. (1979) The role of sediments and bryophytes in phosphorus dynamics in a headwater stream ecosystem. *Limnol. Oceanogr.* **24,** 365–375.

Murphy J. A. and Riley J. P. (1962) A modified single solution method for the determination of inorganic phosphate in natural waters. *Analyt. chim. Acta* **27,** 31–36.

Peverly J. H. (1985) Element accumulation and release by macrophytes in a wetland stream. *J. envir. Qual.* **14,** 137–143.

Reddy K. R. and Patrick W. H. (1984) Nitrogen transformations and loss in flood soils and sediments. *CRC crit. Rev. envir. Control* **13,** 273–309.

Reddy K. R. and Patrick W. H. (1986) Fate of fertilizer nitrogen in the rice root zone. *Soil Sci. Soc. Am. J.* **50,** 649–651.

Sand-Jensen K. and Prahl C. (1982) Oxygen exchange with the lacunae and across leaves and roots of the submerged vascular macrophyte, *Lobelia dortmanna* L. *New Phytol.* **91,** 103–120.

Sand-Jensen K., Prahl C. and Stokholm H. (1982) Oxygen release from roots of submerged aquatic macrophytes. *Oikos* **38,** 349–354.

SAS Institute Inc. (1988) *SAS/STAT User's Guide*, Release 6.03 edition. SAS Institute Inc., Cary, N.C.

Schindler D. W. (1974) Eutrophication and recovery in experimental lakes: implications for lake management. *Science* **184,** 897–899.

Shaw J. F. H. and Prepas E. E. (1990) Exchange of phosphorus from shallow sediments at nine Alberta lakes. *J. envir. Qual.* **19,** 249–256.

Sly P. G. (1988) Interstitial water quality of lake trout spawning habitats. *J. Grt Lakes Res.* **14,** 301–315.

Smith C. S. and Adams M. S. (1986) Phosphorus transfer from sediments by *Myriophyllum spicatum*. *Limnol. Oceanogr.* **31,** 1312–1321.

Smith C. S., Adams M. S., Schmitt M. R. and Adams S. S. (1978) Phosphorus in the water, sediment, and vegetation of the Crojevića River, Montenegro, Yugoslavia. *Verh. int. Verein. Limnol.* **20,** 1536–1542.

Solorzano L. (1969) Determination of ammonia in natural waters by the phenol–hypochlorite method. *Limnol. Oceanogr.* **14,** 799–801.

Sorrell B. K. and Dromgoole F. I. (1987) Oxygen transport in the submerged freshwater macrophyte *Egeria densa* Planch. I. Oxygen production, storage and release. *Aquat. Bot.* **28,** 63–80.

Stainton M. P., Chapel M. J. and Armstrong F. A. J. (1977) *The Chemical Analysis of Freshwater*, 2nd edition. Fish. Envir. Can. Misc. Spec. Publ. 25.

Taylor A. W. and Kunishi H. M. (1971) Phosphate equilibria on stream sediment and soil in a watershed draining an agricultural region. *J. agric. Fd Chem.* **19,** 827–831.

Tessenow U. (1974) Losungs-, Diffusions- und Sorptions-Prozesse in der Oberschicht von Seesedimenten, Part 3. *Arch. Hydrobiol. Suppl.* **47,** 1–79.

Tessenow U. and Baynes Y. (1975) Redox-dependent accumulation of Fe and Mn in a littoral sediment supporting *Isoetes lacustris* L. *Naturwiss.* **672,** 342–343.

Tessenow U. and Baynes Y. (1978) Experimental effects of *Isoetes lacustris* L. on the distribution of Eh, pH, Fe and

Mn in lake sediment. *Verh. int. Verein. Limnol.* **20**, 2358–2362.

Tones P. I., Waite D. T. and Fast D. A. (1980) Report on nutrient impact on the South Saskatchewan river. Saskatchewan Environment, Water Pollution Control Branch.

Werner I. and Weise G. (1982) Biomass production of submersed macrophytes in a selected stretch of the River Zschopau (South GDR) with special regard to orthophosphate incorporation. *Int. Rev. ges. Hydrobiol.* **67**, 45–62.

Westlake D. F. (1961) Aquatic macrophytes and the oxygen balance of running water. *Verh. int. Verein. Limnol.* **14**, 499–504.

Williams J. D. H., Syers J. K. and Walker T. W. (1967) Fractionation of soil inorganic phosphate by a modification of Chang and Jackson's procedure. *Soil Sci. Soc. Am. Proc.* **31**, 736–739.