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NOM DE L'AUTEUR / NAME OF AUTHOR:	Nicole Weinrauch
ADRESSE POSTALE / MAILING ADDRESS:	1407 Nicholson Road Estevan, Saskatchewan S4A 1T6
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WEINRAUCH, Nicole

AUTEUR DE LA THÈSE - AUTHOR OF THESIS

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FACULTÉ, ÉCOLE, DÉPARTEMENT - FACULTY, SCHOOL, DEPARTMENT

TITRE DE LA THÈSE - TITLE OF THE THESIS

**Photosynthesis/Respiration Balance of a Prairie Ecosystem:
North and South Saskatchewan River Watersheds**

Jan Veizer

DIRECTEUR DE LA THÈSE - THESIS SUPERVISOR

EXAMINATEURS DE LA THÈSE - THESIS EXAMINERS

F. Michel

I. Clark

J.-M. De Koninck, Ph.D.

LE DOYEN DE LA FACULTÉ DES ÉTUDES
SUPÉRIEURES ET POSTDOCTORALES

SIGNATURE

DEAN OF THE FACULTY OF GRADUATE
AND POSTDOCTORAL STUDIES

**Photosynthesis/Respiration Balance of a Prairie Ecosystem:
North and South Saskatchewan River Watersheds**

Nicole Weinrauch

**A thesis submitted to the school of Graduate Studies and Research in partial
fulfillment of the requirements for the M.Sc. degree in Earth Sciences**

**Ottawa-Carleton Geoscience Center
Department of Earth Sciences
University of Ottawa
Ottawa, Canada**

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Abstract

The location of the hypothesized “missing carbon sink” has become a subject of open debate in the scientific community, with North America considered to be a prime location for such a sink. While forest ecosystems are considered to be the major candidate, Prairie ecosystems, with their large capacity to store carbon in their soils, may or may not be an ancillary candidate. The North and South Saskatchewan River watersheds are a prime example of such prairie ecosystems and, with this in mind, I attempted to quantify their role as potential sources or sinks of atmospheric CO₂. The sequestration of atmospheric CO₂ by plants via photosynthesis requires that water and CO₂ be utilized at a specific ratio called the water utilization efficiency (WUE). Thus, knowing the hydrological budget of a watershed, specifically the transpiration component, it is possible to calculate its net primary productivity (NPP). This, combined with biological model estimates for heterotrophic soil respiration (R_h), enables evaluation of source and sink tendencies in the watershed. The North and South Saskatchewan River basins were sampled near their mouths for one year and subsequently analysed for $\delta^{18}\text{O}_{\text{H}_2\text{O}}$, $\delta^{18}\text{O}_{\text{DO}}$, δD and $\delta^{13}\text{C}_{\text{DIC}}$. Utilizing these isotopic measurements, meteorological and discharge data enabled quantification of the hydrological budget and the first order estimates of NPP for the watersheds. Of the 52.63 km³ input as precipitation into the North Saskatchewan basin, ~15% is discharged at the river mouth, ~11% is evaporated, ~16% is intercepted and ~58% is transpired. Of the 61.98 km³ input into the South Saskatchewan basin, ~14% is discharged, ~12% is evaporated, ~16% is intercepted and ~58% is transpired. Therefore, transpiration accounts for the majority of the water efflux from both basins. With a WUE of 990 for the North Saskatchewan and 998 for the South Saskatchewan basin, the calculated NPP is 0.0203 and 0.0241 Pg C/a, respectively. These estimates are comparable to model biological estimates of R_h at 0.0204 and 0.0266 Pg C/a, respectively, suggesting that the Saskatchewan Prairie ecosystems are at photosynthetic/respiratory balance and are not a source or sink for atmospheric CO₂. Statistical analysis of water chemistry of both rivers indicated that seasonal variations (discharge, alkalinity, temperature, pH, TDS, $\delta^{18}\text{O}_{\text{H}_2\text{O}}$, δD) and photosynthesis and respiration processes (O₂ saturation, $\delta^{18}\text{O}_{\text{DO}}$, $\delta^{13}\text{C}_{\text{DIC}}$, pCO₂) contributed 75 to 83% to the total variance. pCO₂ levels in the North Saskatchewan River were up to 18 times greater than atmospheric equilibrium values in the ice covered months while those in the South Saskatchewan River were prevented from reaching these magnitudes as the Diefenbaker dam and the Saskatoon weir enabled CO₂ evasion throughout the year. The respiration/photosynthesis ratio remained above 1 for the majority of the year, indicating that the rivers were respiration dominated.

Abstract

La localisation du supposé “missing sink” de carbone est le sujet de nombreux débats parmi les membres de la communauté scientifique, avec l’Amérique du Nord couramment considéré comme étant la localisation primordiale pour un tel «sink». Tandis que les écosystèmes forestiers sont considérés comme étant le candidat par excellence, les écosystèmes de prairie, avec une grande capacité de stockage de carbone dans leurs sols, seraient peut-être un candidat complémentaire. Les bassins versants des rivières North et South Saskatchewan sont de primes exemples de tels écosystèmes de prairie et, tenant compte de ceci, j’ai tenté de quantifier leur rôle en tant que sources ou «sinks» potentiels de CO₂ atmosphérique. La séquestration de CO₂ atmosphérique par les plantes via la photosynthèse requiert que l’eau et le CO₂ soient utilisés dans un rapport spécifique dénommé le «water utilization efficiency» (WUE). Ainsi, en sachant le budget hydrologique d’un bassin versant, et en particulier de la fraction transpiration, il s’avère possible de calculer sa productivité primaire nette (PPN). Ceci, en association avec les estimées de modèles biologiques pour la respiration de sols hétérotrophes (R_h), permet l’évaluation de tendance «source» et «sink» dans le bassin versant. Les bassins des Rivières North et South Saskatchewan fut échantillonnés près de leur embouchure pendant une année, et par la suite analysés pour δ¹⁸O_{H₂O}, δ¹⁸O_{DO}, δD et δ¹³C_{DIC}. L’utilisation de ces mesures isotopiques, ainsi que des données météorologiques et de décharge, a permis la quantification du budget hydrologique et un estimé de premier ordre du PPN pour les bassins versants. Sur les 52.63 km³ de précipitation qui arrivent dans le bassin du North Saskatchewan, ~ 15% est déchargé à l’embouchure de la rivière, ~ 11% est évaporé, ~ 16% est intercepté et ~ 58% est transpiré. Sur les 61.98 km³ qui arrivent dans le bassin du South Saskatchewan, ~ 14% est déchargé, ~ 12% est évaporé, ~ 16% est intercepté et ~ 58% est transpiré. Donc, la transpiration compte pour la grande part des pertes d’eau dans les deux bassins. Avec un WUE de 990 pour le bassin du North Saskatchewan et 998 pour le South Saskatchewan, les PPN calculés sont 0.0203 et 0.0241 Pg C/a, respectivement. Ces estimés sont comparables aux estimés biologiques de R_h à partir de modèles, 0.0204 et 0.0266 Pg C/a, respectivement, ce qui suggère que les systèmes de prairie du Saskatchewan atteignent une balance photosynthèse/respiration, et qu’ils ne seraient ni une source ni un «sink» pour le CO₂ atmosphérique. L’analyse statistique de la chimie de l’eau des deux rivières indique que les variations saisonnières (qui contrôlent la décharge, l’alcalinité, la température, le pH, les TDS, le δ¹⁸O_{H₂O} et le δD) et les processus de photosynthèse et de respiration (refléter dans les valeurs de saturation en O₂, δ¹⁸O_{DO}, δ¹³C_{DIC} et pCO₂) ont contribués de 75 à 83% de la variance totale. Les niveaux de pCO₂ dans le North Saskatchewan étaient jusqu’à 18 fois plus élevés que les valeurs d’équilibre atmosphérique pendant les mois de couvert de glace, tandis que ceux du South Saskatchewan n’arrivaient point à atteindre ces valeurs puisque les barrages Gardiner et Saskatoon permettaient l’échappement du CO₂ tout au long de l’année. Le rapport respiration/photosynthèse est demeurée au-dessus de 1 tout au cours de l’année, indiquant que les rivières étaient dominées par la respiration.

Chapter 1

INTRODUCTION

Global warming and rising concentrations of atmospheric greenhouse gases have become a concern of the scientific and international community and, as a result, of governmental institutions as well. In order to combat increasing levels of atmospheric carbon dioxide and greenhouse gases, several agendas, including the Kyoto, the Hague, Bonn and Johannesburg protocols aim to control and reduce the emission of greenhouse gases. Although these guidelines would aid in reducing CO₂ emissions, there are other greenhouse gases, including water vapour that cannot be controlled or moderated in any way. As water vapour accounts for most of the greenhouse effect, a prudent approach therefore is to look at the interaction and linkages of the water cycle with other greenhouse gases.

CO₂ concentrations have risen from 200 ppmV to 280 ppmV between 18,000 and 10,000 years ago. A comparable concentration increase in CO₂ has taken place subsequently from the 18th Century to the present times (Sundquist, 1993). This latter increase indicates that human activities have greatly changed the concentrations of greenhouse gases in the atmosphere (IPCC, 2001). Evaluation of carbon inventories in the 1980's, while confirming the impact of anthropogenic carbon dioxide emissions, could not account for about one-quarter of the CO₂ released by human activities into the atmosphere (Houghton et al., 1998). Of the 7.1×10^{15} g of carbon released annually, 1.8×10^{15} g is unaccounted for and is currently a subject of vigorous debate and scientific investigation. Some authors (e.g. Ciais et al., 1995) suggest that this "missing carbon sink" is located between 30° N and 60° N latitude, with 70-100% of the CO₂ uptake in North America south of 51° N latitude between June and September (Fan et al., 1988). Sundquist (1993) hypothesized that the sink may involve not only terrestrial plants but also soil components. At present, the boreal forests and bogs of the northern latitudes and the tropical forests of the equatorial regions are both considered to be such potential "missing carbon sinks" (Thompson et al., 1996).

The first step in quantifying carbon sequestration must take into account both the terrestrial and oceanic components. While the ocean itself is a large net carbon sink, with the upper layers experiencing CO₂ mixing with the atmosphere and the deeper layers sequestering the carbon (Sundquist, 1993), the terrestrial component shows signs of both carbon release (output) and capture (input). Global fluxes of CO₂ include anthropogenic sources such as fossil fuel burning and cement production, and natural processes such as forest fires and biotic respiration. CO₂ sinks include carbon sequestration in the deeper ocean and increased photosynthesis.

The atmosphere contains about 730 Pg C (Pg = 10¹⁵ g), with terrestrial photosynthesis/respiration flux on land accounting for ~120 Pg C/a, the oceanic one ~90 Pg C/a and the anthropogenic flux for ~6 Pg C/a (Prentice et al., 2001). The fact that atmospheric CO₂ is recycled via the terrestrial biosphere every six years underscores the importance of terrestrial carbon cycling processes and their impact on the atmospheric CO₂ budget. The flux of CO₂ between the atmosphere and the ocean is almost as large, recycling the atmospheric load in ~8 years. As a result, oceans have absorbed about one-quarter of anthropogenic emissions and only the residual one-quarter has to be sequestered on land. By comparison, the anthropogenic flux accounts for only about 2.5% of the annual flux.

The quantification of global carbon sinks and sources is based on mass balance approaches, but these require reliable inventories of carbon sources and fluxes at a hierarchy of spatial and temporal scales, a requirement not generally met at present. Telmer and Veizer (2000, 2001) proposed an alternative approach that may enable *first order estimates* of photosynthetic consumption of CO₂ on watershed scales. These can be compared with biologically estimated respiration fluxes, thus permitting to test whether a given watershed is a net source or sink of CO₂.

Photosynthetic activities of biota act as a sink, consuming CO₂ from the atmosphere and subsequently lowering its concentrations, while respiration works in the opposite direction, releasing the CO₂ and increasing the level in the atmosphere. Note that a decrease in respiration without an increase in photosynthesis may also account for a decline in atmospheric CO₂ concentration and vice versa (Flanagan and Ehleringer, 1998). The net CO₂ fluxes are a result of heterotrophic soil respiration versus the net

primary productivity (NPP). However, the NPP is dependent not only on CO₂, but also on the availability of water (Lovett, 2002; Nemani et al., 2002). This relationship, expressed as Water Utilization Efficiency (WUE), maintains that a plant has to transpire almost 1000 units of water to sequester one unit of CO₂. Thus knowing the hydrological budget of a spatial entity (i.e. a watershed), it is possible to estimate its NPP. Comparison of this value to heterotrophic soil respiration enables us to interpret the source or sink capacity. In this work, a decadal scale is utilized because heterotrophic respiration lags behind changes in NPP (Thompson et al., 1996). I utilize this approach for the Canadian Prairie ecosystem in order to estimate its net ecosystem productivity (NEP) (Buchmann and Schulze, 1999).

Earlier studies of the "missing carbon sink" problem dealt with large scale temperate or tropical forested regions such as the Mississippi or the Amazon River basins (Lee and Veizer, in press; Richey et al., 2002), because of the large quantities of woody vegetation, thick forest floor cover and low carbon turnover times in the soils, all enhancing the CO₂ sequestration (Thompson et al., 1996). By contrast, the Prairie and grassland systems have little woody vegetation and sparse leaf cover, although C₃ grasses and agricultural crops are plentiful (Archibold, 1995). As a result, the soils are exposed and the interaction with the atmosphere is comparatively unimpeded. Such areas, with low turnover times and low NPP, do not seem to contribute much to the missing sink (Thompson et al., 1996), but this is debatable because grasslands store most of their carbon in the soils, with turnover times anywhere between 10 and 10,000 years (Hall et al., 2000). In order to test this idea, the present study concentrates on the North and South Saskatchewan River watersheds. The South Saskatchewan River basin is primarily prairie grassland while the North Saskatchewan River basin consists of prairie grassland, aspen parkland and boreal forest. In terms of their yearly temperature and precipitation values, the average of both basins lie at the intersection of the grassland and boreal domains (Figure 1), and can be classified as a cool Prairie ecosystem with near boreal forest characteristics.

The objectives of this thesis are twofold. The first objective is to use a methodology similar to that in Lee and Veizer (in press) and Telmer and Veizer (2000; 2001) to estimate first order fluxes of carbon dioxide in a semi-arid prairie dominated

watershed. Secondly, utilizing the methodology of Quay et al. (1995), the aquatic respiration/photosynthesis ratios for both river systems are quantified. In general terms, the hydrological budget discussed here is an overview of the entire Saskatchewan River basins, while the respiration/photosynthesis chapter deals mostly with the aquatic aspects of the basins.

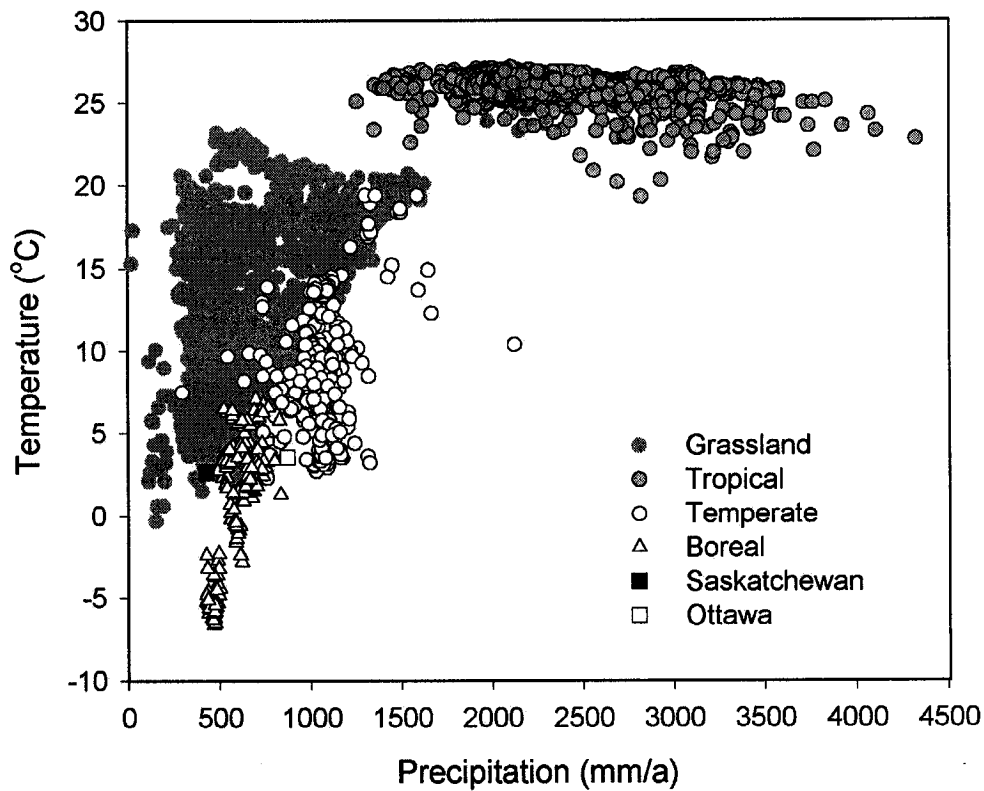


Figure 1: Temperature and precipitation characteristics of four major ecosystems. (Global Primary Production Data Initiative (GPPDI) Grid Cells NPP Dataset; Zheng et. al. (2001)). Saskatchewan and Ottawa watersheds are plotted on the grid for comparison. Ottawa data from Telmer (1997) and Telmer and Veizer (2000).

Chapter 2

THE NORTH AND SOUTH SASKATCHEWAN WATERSHEDS

2.1 Geology

The North and South Saskatchewan River basins are located in Western Canada and encompass most of the lower and central portions of Alberta and Saskatchewan, with a very small area extending into northern Montana (Figure 2). The basins are bounded by the coordinates 55°N, -118°W and 48°N, -105°W. These coordinates confine all data sets discussed in this manuscript.

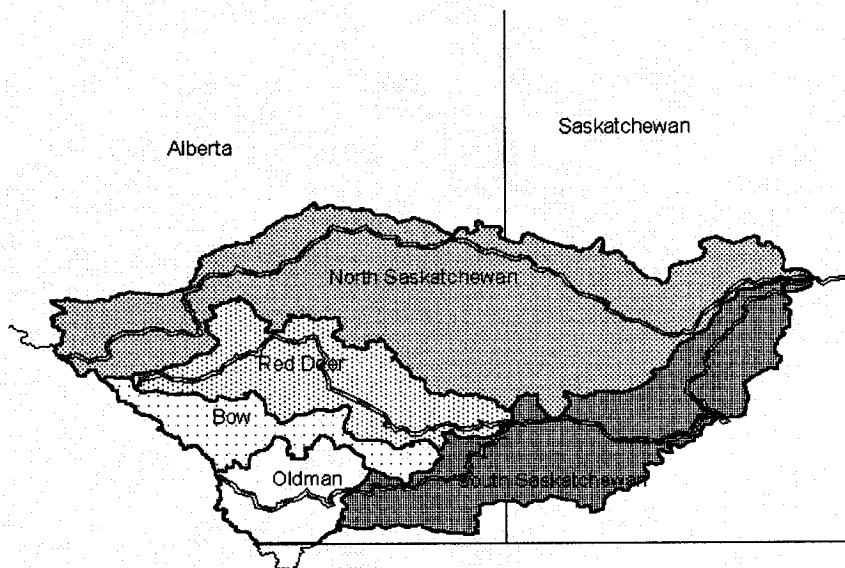


Figure 2: North and South Saskatchewan watershed boundaries. The South Saskatchewan is subdivided into the sub-basins of Oldman River, Red Deer River, Bow River and the South Saskatchewan River. The North Saskatchewan basin is regarded as a single unit.

The provinces of Saskatchewan and Alberta (excluding the mountainous zone) are characterized by flat lying, nearly horizontal geologic strata, with a gradual elevation decrease from west to east. Cretaceous carbonate formations underlie most of the basins, with the surficial geology dominated by glacial till, which reach thicknesses of hundreds of meters, and constitute a large proportion of the exposed surface. The till also fills the previously eroded river valleys and basins, resulting in a low relief terrain from central Alberta to Manitoba. As a result, topographical features are subdued. The emphasis in this section will be placed on the more recent geological events as they predominantly shaped the present surface and have the greatest impact on the river systems of today.

The Rocky Mountain Range comprises the western border of the basins and trends northwest to southeast across the Canadian-American border. The mountains themselves are comprised of crustal fragments that have been accreted onto the existing cratonic mass and then displaced in a northwest to southeast fashion along the strike-slip faults (Clague, 1991). The mountains are of Proterozoic to Cretaceous age and overlie unmetamorphosed sedimentary rocks averaging 4,500 meters in thickness (Scott and Klassen, 1993).

Thick deposits of Phanerozoic rocks overlie the crystalline basement rocks of the basin east of the mountains. These deposits reach up to 5,000 meters in thickness in the western parts of the basin and thin eastward into central Saskatchewan to a thickness of 1,200 to 1,800 meters (Scott and Aitken, 1993). The Palaeozoic portion consists primarily of stacked carbonate and evaporite units (Last, 1999). A thick deposit of Cretaceous shale, siltstone and sandstone lies near the top of these Phanerozoic rocks. Some Tertiary deposits are exposed on the western edge of the basins, and may be found capping hills and plateaux. This is due to the increased resistivity to weathering compared to the surrounding Cretaceous deposits (Klassen, 1989).

The surficial area eastwards of the Rocky Mountains is divided into several zones, including the Cordilleran Fold Belt, the Foothills Belt and the Interior Plains. The Cordilleran Fold Belt extends along the eastern edge of the mountains. It varies from approximately 100 to 400 meters in width, tapering out in the higher latitudes towards Peace River. This Belt consists of Palaeozoic carbonates and clastics exposed in the thrust zones and folds produced by the tectonic activity in the late Jurassic/early Tertiary.

This tectonic activity resulted in little metamorphism and no plutonism (Scott and Aitken, 1993).

The Foothills Belt lies further east, parallel to the Cordilleran Fold Belt. This area is underlain by deformed Mesozoic and Tertiary clastics with upper Palaeozoic carbonates and Mesozoic sandstones exposed at some of the higher elevations due to thrusting and folding events (Scott and Aitken, 1993; Scott and Klassen, 1993). Subsequently, the eastward flowing Laurentide ice sheet covered the entire Foothills region, excluding its southwest corner, leaving thick sedimentary deposits in the valleys and basins created by the folding (Fulton, 1989; Dawson, 1992). This area is very important to the hydrology of the basins as the headwaters of the North Saskatchewan, Red Deer, Oldman and Bow Rivers originate here.

The Interior Plains, divided into the Alberta and Saskatchewan Plains, cover most of the North and South Saskatchewan Basins. The plains are underlain by the large Interior Platform, a wedge of sedimentary rock, primarily carbonates, approximately 6 kilometres thick, tapering out towards the northeast. Underlying the Platform are flat lying Proterozoic rocks (Scott and Aitken, 1993). The Alberta Plains primarily consist of Cretaceous sediments, approximately 800 to 1,000 meters thick, with the elevated landmasses topped by Tertiary sediments. The Saskatchewan Plains also contain Cretaceous beds, 400 to 800 meters thick, and show the greatest impact of recent glacial episodes (Scott and Klassen, 1993).

2.2 Glaciation

Two major glacial episodes, the Cordilleran and the Laurentide, influenced the topography of the North and South Saskatchewan River basins. The two glaciers began advancing approximately 40,000-30,000 BP and disappeared by 6,500-10,000 BP (Dawson, 1992). The advancing glaciers extensively scoured large areas of predominantly Tertiary sediments. The subsequent retreat of the glaciers re-worked and redeposited these sediments, covering the area with thick till and moraine sediments.

The Cordilleran ice sheet affected the most western parts of the basins and covered British Columbia, northern Alberta and the Rocky Mountains. The ice sheet

originated in the ice cap of the mountains and moved laterally downward along the cliffs, eventually terminating within the Foothills area. Valleys that were parallel to the movement of the ice flow direction sustained extensive scouring and sediment removal (Clague, 1991). Most of the surface sediments present in this area today are a direct result of this glaciation.

The Laurentide ice sheet dominated the rest of the Prairie region. Several ice domes in northern Canada expanded over time and the resultant ice sheets extended southwest across 4,400 km of North America, reaching the Foothills region and eventually encountering the edge of the Cordilleran ice sheet. The ice sheets eventually merged on the eastern side of the mountains and covered more than 16 million km². Subsequently, between 20,000-21,000 BP, areas of the Laurentide ice sheet reached a maximum thickness of 3000 meters and the Cordilleran ice sheet began its retreat (Dawson, 1992). Both ice sheets disappeared by 10,000 and 6,500 BP, respectively (Fulton, 1989; Dawson, 1992), leaving behind extensive sedimentary cover including large till and moraine deposits.

Glacial episodes fashioned the present day landscape with moraines and irregular till mounds dominating the landscape. Much of the surface is covered with glacial drift ranging in thickness from 50 to 200 meters. As a result, most of the bedrock topography is subdued or not reflected at all in the surface topography. The modern river valley systems are a direct result of the infilling of the pre-existing valleys, with the retreating glaciers carving out successor valleys and basins (Klassen, 1989).

2.3 Climatology and physiographic setting

The North and South Saskatchewan watersheds are sub-basins of the Saskatchewan River basin, which, in turn, is part of the larger Nelson River system. The North Saskatchewan basin is commonly considered to be one cohesive unit, although some institutions may subdivide it into the North Saskatchewan and Battle River sub-basins (PFRA, 2002). The South Saskatchewan River basin is subdivided into the Bow, Oldman, Red Deer and South Saskatchewan watersheds. All four sub-basins are in

Alberta, with only the South Saskatchewan River extending into Saskatchewan (PFRA, 2002).

The North Saskatchewan River is 1,287 km long and drains an area of 122,800 km². It flows from west to east, originating in the Saskatchewan Glacier, the ice fields of the national parks of western Alberta. Several smaller rivers drain into the main channel, including the Brazeau, Clearwater, Vermillion and Battle, the latter being the only one with any significant water contribution (Alberta Environment, 2000). The North Saskatchewan River passes through several major urban centres, including Edmonton, the Battlefords and Prince Albert, and finally joins the South Saskatchewan River about 60 km east of Prince Albert, becoming the larger Saskatchewan River (Alberta Environment, 2000; The Columbia Encyclopedia, 2001). At its confluence, the North Saskatchewan discharges 7.73 km³ annually. The mean annual temperature of the basin is 2.2°C while the mean annual precipitation is 449 mm (Legates and Wilmott, 1990; Wilmott and Matsuura, 2001).

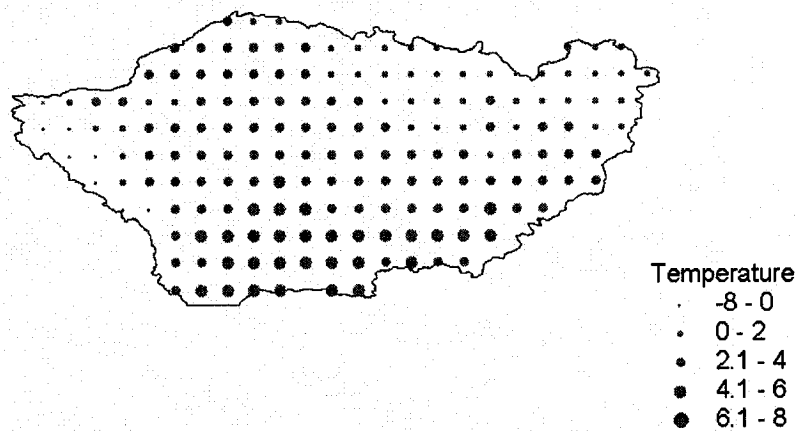


Figure 3: Average 30-year temperatures over the basins. Temperature measurements are given in degrees Celsius. (Data from <http://lwf.ncdc.noaa.gov/oa/climate/research/ghcn/ghcngrid.html>)

The South Saskatchewan River is 1,390 km long and drains an area of 144,300 km². The South Saskatchewan River primarily derives from the confluence of the Bow and Oldman Rivers and flows northeast, passing through agricultural areas and extensive

flat prairie regions until its confluence with the North Saskatchewan River (Alberta Environment, 2000; The Columbia Encyclopedia, 2001). At this point, the South Saskatchewan River discharges 8.83 km³ annually. The mean annual temperature in the South Saskatchewan Basin is 2.6°C and the mean annual precipitation is 475 mm (Legates and Wilmott, 1990; Wilmott and Matsuura, 2001).

Temperature and precipitation trends are similar for both basins. Average temperature decreases from the east to the west and from the south to the north. Drops in temperature coincide closely with the change of the Prairies into aspen parklands in the northern portions of the North Saskatchewan River basin, and with the mountainous zones on the western border of the basins (Figure 3). Precipitation increases from the east to the west and from the centre of the basins towards the outer edges. The large, dry Prairie region shows the lowest and least variable precipitation (Figure 4).

Most of the North and South Saskatchewan River basins lie within an area unique to the North American prairies known as “Palliser’s Triangle”. This region is the driest area of the northern prairies and extends from Manitoba and Saskatchewan into Alberta, covering the southern and south-central regions of the provinces (International Institute for Sustainable Development and Environmental Adaptation Research Group, 1997). It is characterized by cycles of extreme aridity, often resulting in droughts. Twenty serious droughts were recorded in the nineteenth century and over ten in the twentieth century (Godwin, 1986).

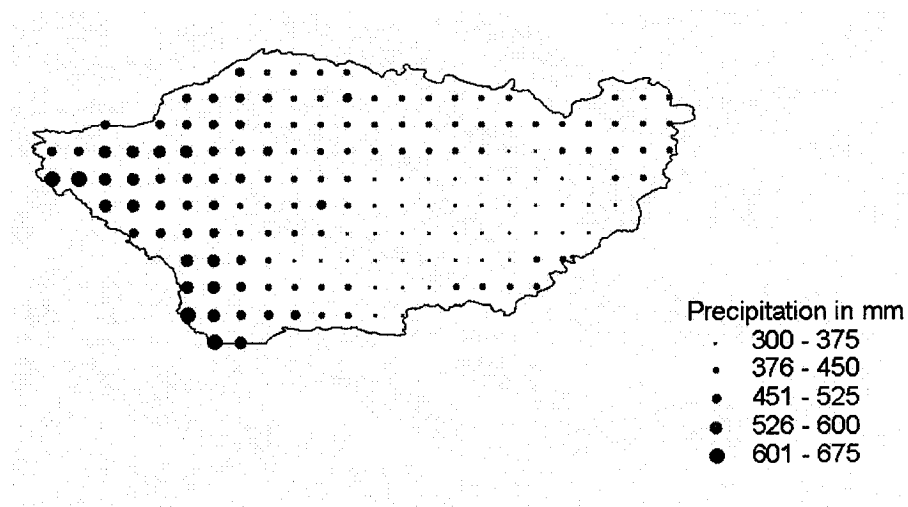


Figure 4: Average 30-year precipitation over the basins. Precipitation measurements are given in mm/year. (Data from <ftp://daac.gsfc.nasa.gov/data/hydrology/precip/legates>)

Chapter 3

SAMPLES AND ANALYTICAL PROCEDURES

3.1 Sampling sites and frequency

Sampling on the North Saskatchewan River took place at the civic boat launch in the city of Prince Albert, Saskatchewan, and on the South Saskatchewan River at the Weldon ferry crossing approximately 60-70 km east of Prince Albert. Both sampling locations were upstream of the confluence into the Saskatchewan River.

Sampling commenced in September 2000 and ended in August 2001. Sampling was conducted on a bi-weekly basis. However, in April, sampling frequency was increased to a weekly basis in order to record any isotopic changes in water composition from snowmelt and associated runoff as well as during the increased flow volume during the spring. Winter sampling was conducted bi-weekly or less frequently if adverse climatic conditions or dangerous ice conditions prevailed. In the winter a gas powered ice auger was used to drill a thirty-centimeter hole through the solid layer to the free flowing water beneath. Any remaining ice slurry was removed with a metal sieve, thereby leaving the water samples free of ice.

3.2 Field sampling and measurements

Water samples were collected in three different types of bottles: pre-washed VWRbrand™ TraceClean™ 40 mL amber glass vials with Teflon/silicone septa open-topped caps, pre-washed VWRbrand™ TraceClean™ 125 mL amber glass bottles with Teflon lined solid-top caps, and 125 mL evacuated serum bottles (Wheaton # 2725). The TraceClean™ and the serum bottles had greater than 100 µl saturated HgCl₂ added as a bactericide prior to sampling. The serum bottles were crimp sealed with butyl blue

septum (Bellco Biological Glassware, Vineland, NJ) that had been pre-washed (0.1 NaOH then distilled H₂O), dried and sterilized.

Water samples for δD and $\delta^{18}O_{H_2O}$ were collected by rinsing a syringe three times with river water, immersing it in the river, tipping it upward to release any captured air and inserting the plunger under water. These samples were field filtered through 0.45 μm membranes and stored in the VWRbrand™ TraceClean™ 40 mL amber glass vials. These samples were not preserved in any way.

Water samples for $\delta^{13}C_{DIC}$ (dissolved inorganic carbon) from September to January were collected in VWRbrand™ TraceClean™ 125 mL amber glass bottles in a method similar to that of δD and $\delta^{18}O_{H_2O}$. From February to August, $\delta^{13}C_{DIC}$ samples were collected in VWRbrand™ TraceClean™ 40 mL amber glass vials to accommodate an alternate laboratory analysis method. All $\delta^{13}C_{DIC}$ samples were preserved with HgCl₂ to prevent any biological activity.

Water samples for $\delta^{18}O_{DO}$ (dissolved oxygen) were collected by inverting and immersing the evacuated serum bottles into the river, after which a 0.25 gauge needle was inserted through the septum beneath the water and then extracted after the bottles were filled. Oxygen degassed from the water as the bottle was being filled and produced a small headspace for analysis (Wassenaar and Koehler, 1999). These samples were not filtered but they were preserved with HgCl₂.

Field measurements consisted of pH, alkalinity, temperature, total dissolved solids (TDS), and dissolved oxygen content. From September to April, pH, temperature, dissolved oxygen and total dissolved solids field measurements were conducted using a Hydrolab™ DataSonde Series 4a calibrated in 100% humidity. The dissolved oxygen readings are calibrated according to temperature and barometric pressure. From May until August, field measurements were made with two separate instruments. Temperature and dissolved oxygen content were taken using an YSI™ 85 Dissolved Oxygen Handheld Probe that was calibrated according to elevation and salinity prior to each use.

pH and temperature were directly measured with a HACH One™ combination pH electrode. The probe was calibrated before each use with pH 7.0 and 10.0 solutions and confirmed after the sample reading with an 8.4 solution. Precision was ± 0.3 .

Alkalinity measurements were performed in the field using a HACH digital titrator (model 169000-01) by combining 100 mL of sample with Bromcresol green-methyl red indicator and titrating with 1.6 N sulphuric acid. Alkalinity was measured as CaCO_3 and later converted to the more common HCO_3^- for calculations and interpretations. Precision for alkalinity is ± 5.9 . All HACH equipment information and procedures can be found in the HACH Water Analysis Handbook (1989).

3.3 Laboratory measurements

All samples were measured for isotopes as soon as possible after being collected. δD , $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ and $\delta^{13}\text{C}_{\text{DIC}}$ were all measured at the G.G. Hatch Isotope Laboratory at the University of Ottawa. $\delta^{18}\text{O}_{\text{DO}}$ samples were measured at the National Water Research Institute at Innovation Place on the University of Saskatchewan campus.

Water samples for δD measurements collected between September and December 2000 were prepared by reducing water samples using zinc outlined in the method by Coleman et al. (1982). Approximately 100 mg of zinc was dried in a break seal under vacuum using a small acetylene torch. Three microlitres of sample were injected, drawn into the break seal via liquid nitrogen, sealed and subsequently reacted with the zinc at 500°C . The gas was then analysed on a double collector Micromass VG 602E mass spectrometer (Coleman et al., 1982). Reproducibility was $\pm 1.5\%$. The δD for samples collected from January to September 2001 were measured via a liquid autosampler attached to an Optima coupled with an elemental analyser used in vacuum with chrome packing. The chromium reduction method reduces fractionation effects because the isotope ratio is measured immediately after the reaction occurs (Brand et al., 1996). Reproducibility was $\pm 2.0\%$.

Samples for $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ were prepared according to the method of Epstein and Mayeda (1953). One millilitre of sample was placed in a small glass vial that was attached to an automated shaker, equilibrated with gaseous CO_2 at 25°C for six-hours and analyzed on a triple collector VG SIRA 12 mass spectrometer. Eighteen samples and two standards were analysed with every sample session. Reproducibility was $\pm 0.1\%$.

$\delta^{13}\text{C}_{\text{DIC}}$ for samples from September to December 2000 were measured offline using extraction by phosphoric acid combined with liquid nitrogen and -80°C ethanol traps. The resulting CO_2 gas was trapped in an evacuated break seal and analysed on a triple collector VG SIRA 12 mass spectrometer. Reproducibility was $\pm 0.1\%$. DIC samples collected from January to September 2001 were measured online using a Total Carbon Analyser (O.I. Analytical Model 1010) interfaced with a Finnigan Mat Delta PlusTM mass spectrometer. Water samples were loaded in their original sample vial on a rotating tray with an automated system, where the sample volume was proportional to DIC concentrations (ppm C) (St. Jean, personal communication). Reproducibility was $\pm 0.5\%$.

The $\delta^{18}\text{O}$ of dissolved oxygen was measured from an aliquot taken from the headspace generated during the sampling. Water samples were over-pressured with helium gas and 5 mL of water was removed. Subsequent agitation displaced oxygen from the sample into the headspace. An aliquot of gas from the headspace was then analysed for $\delta^{18}\text{O}_{\text{DO}}$ by continuous flow isotope-ratio mass spectrometry using a Micromass Optima (Wassenaar and Koehler, 1999). Reproducibility was $\pm 0.17\%$.

All results are expressed in the standard delta per mil notation (δ -‰).

$$\delta\text{-‰} = [(R_{\text{sample}}/R_{\text{standard}}) - 1] \times 1000 \quad \text{where} \quad (1)$$

R=heavier isotope/lighter isotope ratio

For example:

$$\delta^{18}\text{O}_{\text{sample}} \text{‰} = [({}^{18}\text{O}/{}^{16}\text{O})_{\text{sample}} / ({}^{18}\text{O}/{}^{16}\text{O})_{\text{standard}} - 1] \times 1000 \quad (2)$$

Results are reported relative to a predetermined reference standard, in this case the Vienna Standard Mean Ocean Water (VSMOW) for oxygen and hydrogen and Vienna Pee Dee Belemnite (VPDB) for carbon.

Chapter 4

HYDROLOGICAL BUDGETS OF THE NORTH AND SOUTH SASKATCHEWAN WATERSHEDS

4.1 General considerations

The terrestrial carbon and water cycles are coupled via photosynthetic and respiratory processes of plants, algae and, to a lesser extent, animals. By measuring the fluxes of water and carbon between the biosphere, hydrosphere and atmosphere, we can provide a first order approximation of the magnitude and direction of carbon fluxes, and thereby potentially pinpoint the geographical areas of greatest carbon sequestration and release. The greatest fluxes are generally assumed to be associated with the forests of the northern latitudes and the tropical forests of the equatorial latitudes (Ciais et al., 1995; Prentice et al., 2001). It is also believed that these ecosystems may represent the locations of greatest sequestering of atmospheric CO₂, the theorized “missing carbon sink”. Recent evidence casts doubt on these assumptions, because field studies appear to indicate either an equivalency of photosynthesis/respiration or variable relationships (Luo et al., 2001; Richey et al., 2002). By measuring the hydrometric fluxes of a watershed, we can theoretically calculate the approximate photosynthetic flux, which can be compared to the respiration flux determined by other techniques. This enables us to determine whether the watershed is a source or a sink for CO₂.

The hydrological budget of a watershed can be solved with a common, simplified equation:

$$A = O + \Delta S \quad (3)$$

where A is the total input, O is the output and ΔS is the change in groundwater storage. The input (A) is equivalent to precipitation (P) and the inflow from other rivers (if they lie outside of and flow into the basin), while the output (O) is equivalent to the discharge

of water out of the basin (Q) plus evapotranspiration (ET). When the basin's budgets are analysed and averaged over a long time period (30 year dataset used in this study), the infiltration and changes in groundwater storage values (ΔS) become zero, as the periodic fluxes over time will cancel each other. It is assumed that groundwater removal for irrigation purposes will, over the period of time encompassed by the databases used in this thesis, be returned through infiltration, evaporation and precipitation and overland flow to the basins and that any changes will also cancel each other. Also, if the rivers' headwaters originate within the basin, then there is no input from external river sources. Thus, this value would also become zero. The approach based on long term averages holds well when applied to lakes and is therefore conceivably valid also for watersheds (Black, 1990; Fetter, 2000). Based on these qualifications, equation (3) can then be defined as:

$$P = ET + Q \quad (4)$$

The precipitation (P) and discharge (Q) variables in equation (4) can be calculated by using the Legates and Wilmott (1990) and Vörösmarty et al. (1998) databases that can be found in Appendix 1. Evapotranspiration is then simply the difference between P and Q.

Evapotranspiration is complex and difficult, if not impossible, to measure directly. The term has to be subdivided into its evaporation (E), transpiration (T) and interception (I) components, resulting in the equation:

$$ET = E + T + I \quad (5)$$

The variables ET, E and I can be measured or calculated, permitting the evaluation of the transpiration flux and then, utilizing the WUE, the photosynthetic flux of carbon.

Evaporation can be directly measured in several ways. Rain gauges are most commonly utilized and the techniques regarding them are continually being improved (Gibson and Edwards, 1999; Gibson et al., 1999). However, these methods can be time consuming and expensive. Fortunately, evaporation and sublimation processes result in the fractionation of hydrogen and oxygen isotopes while transpiration and interception

processes do not (Mosler and Stichler, 1975; Gat and Matsui, 1991). On this basis, evaporation can be separated from the rest of the evapotranspiration term and calculated via isotopic mass balance equations. Sublimation is encompassed within the evaporation term.

During a precipitation event, one of three things happens. The water can be caught and held by the foliage until it evaporates, it can flow off the leaves and stems to the ground (stem flow), or it can pass directly to the earth with no interference. Interception is the amount of precipitation prevented from reaching the ground by vegetative cover and constitutes a significant portion of the evapotranspiration term in the hydrological budget. Stem flow accounts for less than 2% of the total annual precipitation (Brooks et al., 1997) and will be considered within the interception term. Interception values are difficult to determine because they are based on leaf area index, stem diameter, precipitation quantity and wind speeds (Heatherington, 1987; Brooks et al., 1997). Therefore, a range of values has been claimed for different types of land cover. Although forests are considered to have the highest interception values, even arid and semi-arid environments (including the prairies) with sparser vegetation, such as grass and shrubs, can intercept up to 10-20 % of precipitation (Brooks et al., 1997).

Transpiration is the release of water vapour back into the atmosphere through the stomata, or small pores, of leaves. It is the crucial term for calculation of the net primary productivity of the basins. Transpiration (T) is the calculated difference between evapotranspiration (ET), evaporation (E), and interception (I).

4.2 Precipitation flux

Global precipitation data for the North and South Saskatchewan River basins was obtained from Legates and Wilmott (1990) and covered 60 years, from 1920-1980. Terrestrial measurements were taken using gauges and missing data was interpolated, resulting in a $0.5^\circ \times 0.5^\circ$ latitude-longitude grid. The data was then clipped according to the watershed boundaries used in this study. Seasonal variations are distinct with the lowest volumes of precipitation in February in both basins (16 and 27 mm/month) and the highest in June (77 and 73 mm/month) for the North and South Saskatchewan,

respectively. The warmer season, from May to October, shows higher average precipitation, with 53 and 47 mm/month while the colder season, from November until April, shows a much lower volume, averaging 21 and 32 mm/month for the North and South Saskatchewan, respectively. Yearly, the entire area averages 464.5 mm with an average of 449 mm in the North and 475 mm in the South (see Figure 5).

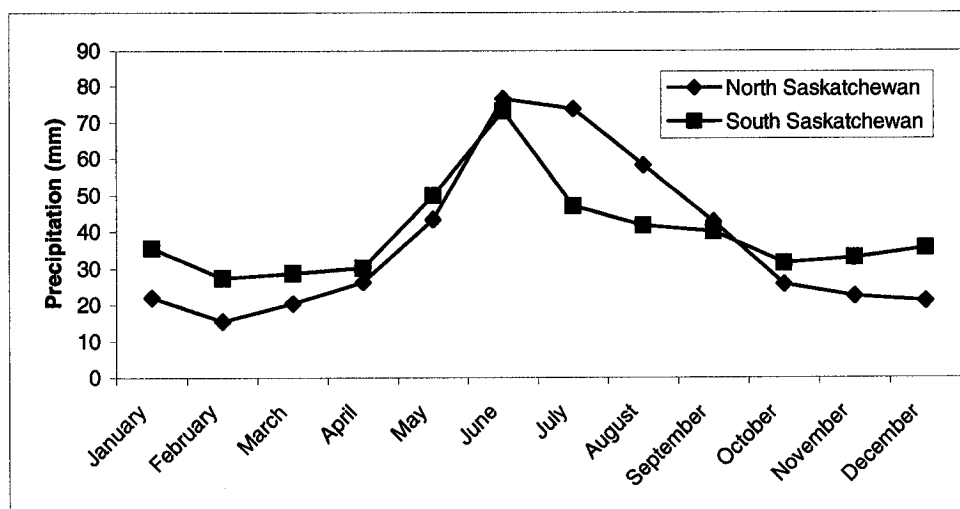


Figure 5: Average monthly precipitation for the North and South Saskatchewan watersheds.

4.2.1 Stable isotopic composition of precipitation

The evaporation component of the evapotranspiration flux in this study was derived from isotopic fractionation of precipitation and the discharge flux. It is therefore essential to discuss the oxygen and hydrogen isotopic systematics of precipitation first.

The isotopic composition of continental precipitation is influenced by latitude, altitude and ocean proximity (Dansgaard, 1964). High latitude and/or high altitude precipitation is characterized by more negative $\delta^{18}\text{O}$ and δD . Additionally, more rainout occurs as the moisture mass reaches further inland, depleting it in ^{18}O and D (Clark and Fritz, 1997). All of these modifiers are temperature dependent, with high latitudes and increasing altitudes resulting in increased condensation and subsequent rainfall events. Temperature also controls the isotopic fractionation factor, thereby controlling the degree

of fractionation between the moisture source and precipitation (Hoefs, 1987), with colder temperatures resulting in greater fractionation. Additionally, inland precipitation is greatly influenced by seasonal events, primarily temperature fluctuations, the source of the moisture mass and the absence of the isotopic buffering effects produced by the ocean.

The North and South Saskatchewan basins are interior continental and, therefore, all these effects affect the isotopic composition. Both river basins are located at high latitudes (48°N to 55°N), with the Rocky Mountains generating a rain shadow for the moisture coming from the Pacific Ocean to the west. Storm events from the north and west are therefore relatively depleted in ^{18}O and D as compared to those from the south and east (Brown, 1970). While the incursions of Gulf and Arctic air masses in the summer and winter months may happen, the primary sources of moisture in the basin are the air masses moving over the mountains from the Pacific Ocean (Bryson and Hare, 1974; Fritz et al., 1987).

The average stable isotopic composition of global precipitation is estimated at $\delta^{18}\text{O} = -4\text{‰}$ and $\delta\text{D} = -22\text{‰}$ (Craig and Gordon, 1965). However, geographically, the $\delta^{18}\text{O}$ and δD of precipitation is seasonally variable. The covariation of the hydrogen and oxygen isotopes gives a highly correlated trend called the Global Meteoric Water Line (GMWL). The equation for the GMWL is $\delta\text{D} = 8 * \delta^{18}\text{O} + 10$ and has been established by averaging a large number of local meteoric water lines from all over the globe over the past 50 years (Craig, 1961). Presently, a more accurate equation based on the isotopic precipitation data from the International Atomic Energy Agency (IAEA/WMO, 2001) for the GMWL would be $\delta\text{D} = 8.16 * \delta^{18}\text{O} + 10.35$ (Rozanski et al., 1993). The Local Meteoric Water Line (LMWL) for North America is $\delta\text{D} = 7.95 * \delta^{18}\text{O} + 6.03$ (Yurtsever and Gat, 1981), while the Canadian MWL (CMWL) is $\delta\text{D} = 7.75 * \delta^{18}\text{O} + 9.83$ (Fritz et al., 1987), both only slightly different from the GMWL. This similarity to the GMWL may be attributed to the fact that 40% of the samples used to construct the GMWL originate from North America (Craig, 1961; IAEA/WMO, 2001).

The western and eastern regions of Canada have somewhat different LMWL, resulting in lower intercepts in the western regions (Fritz et al., 1987;

http://www.sciborg.uwaterloo.ca/research_groups/eilab/gnip/maps&animations/index.

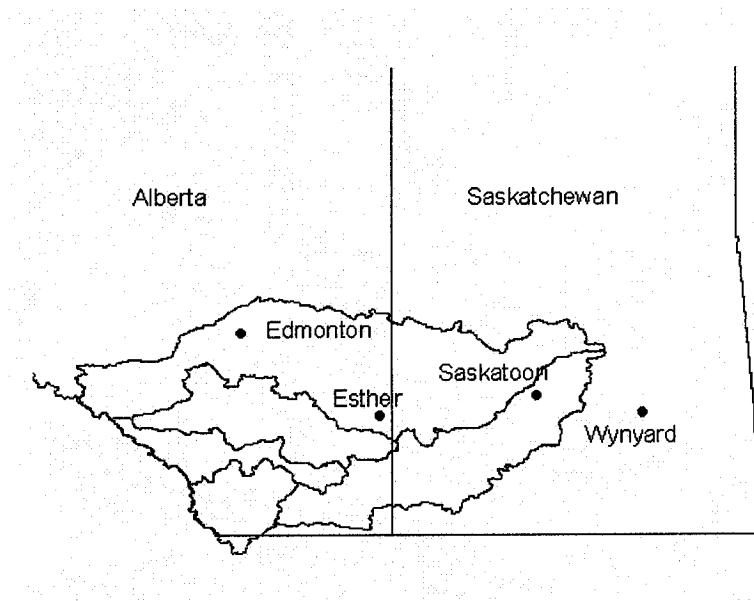


Figure 6: Location of GNIP and Environment Canada precipitation sampling stations. Edmonton, Wynyard and Esther have been maintained by IAEA/WMO, the Global Network of Isotopes in Precipitation (2000) section, for nine, seven and three years, respectively, while Saskatoon has been independently maintained by Environment Canada (2002) for twelve years.

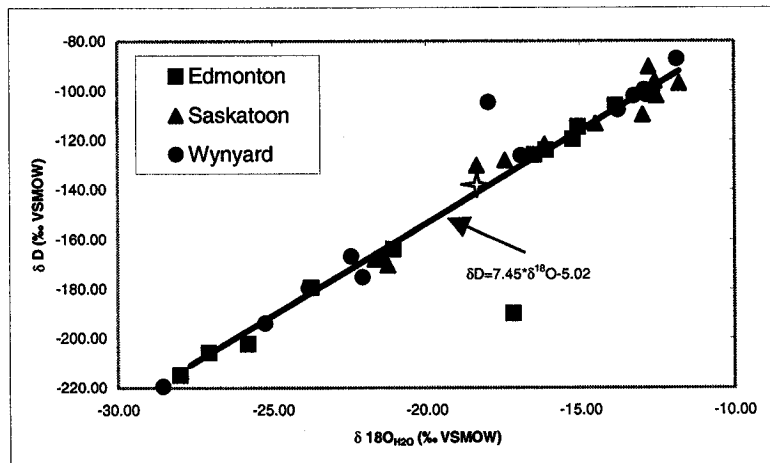
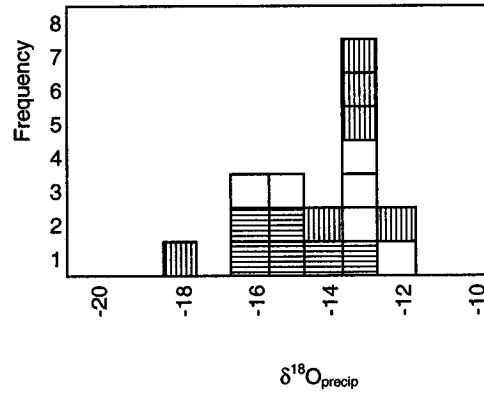


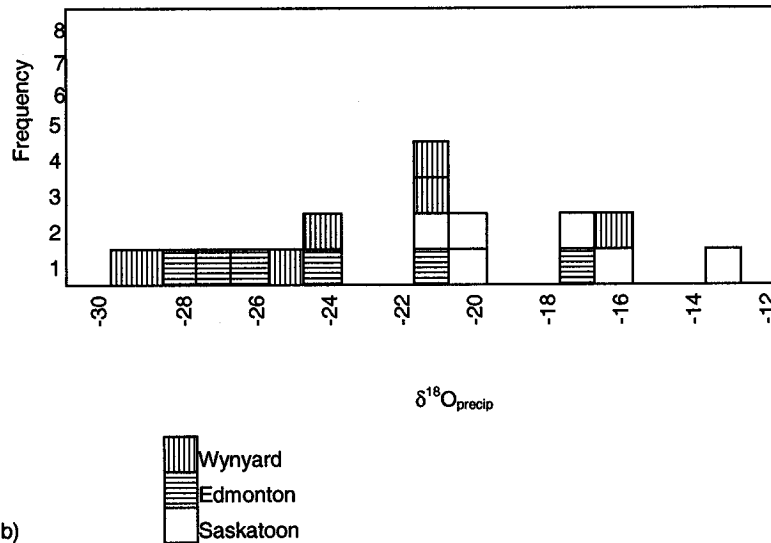
Figure 7: Calculated averaged monthly data for primary precipitation sampling stations. Star denotes the average non-weighted average isotopic composition of precipitation.

Summer



a)

Winter



b)

Figure 8: Seasonal $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ histograms based on a) summer (May to October) and b) winter (November to April).

html#North%20America). For this study, the precipitation monitoring stations found within or in close proximity to the Saskatchewan River basins were recalculated and averaged into three MWL's. These stations are Edmonton, Wynyard (data from IAEA/WMO, 2001) and Saskatoon (Wassenaar, 2002, unpublished data) (see Figure 6 for locations). Multiple years of data for each station were averaged into monthly units. The three MWL's produced were then averaged into a local meteoric water line (Figure 7). Edmonton, located in the North Saskatchewan Basin, has a MWL of $\delta\text{D}=7.22*\delta^{18}\text{O}-14.09$, Saskatoon, located in the South Saskatchewan Basin, $\delta\text{D}=7.46*\delta^{18}\text{O}-4.10$ and Wynyard, located just east of the basins, $\delta\text{D}=7.67*\delta^{18}\text{O}+3.12$. The average $\delta^{18}\text{O}$ and δD

of the local precipitation is -18‰ and -139‰ , respectively. A fourth station, Esther, was located in the centre of the region, but was not used because of the paucity of the measurements.

The three stations combined produced a LMWL with the equation $\delta D = 7.45 * \delta^{18}O - 5.02$. This MWL has a similar slope but very different intercept than the CMWL. Western Canada contains the prairie ecosystem, which is a semi-arid environment, so secondary evaporation of falling raindrops may have influenced the LMWL, causing lower intercepts and shallower slopes (Fritz et al., 1987). Also, the lower intercept may be related to the moisture source's (the Pacific air mass) influence on this region, primary and secondary evaporation, or to equilibration with the local humidity (Ingraham, 1998).

Grouping precipitation data into May to October and November to April, strong seasonal trends become evident (Figure 8), with more negative isotopic values ($-21 \pm 9\text{‰}$) in the cold season than in the warm one ($-15 \pm 3\text{‰}$). On average, the $\delta^{18}O_{H_2O}$ and δD values of precipitation of the South Saskatchewan River basin are more positive (Figure 8) than the North Saskatchewan watershed, owing to the more southerly location of the former.

4.2.2 Stable Isotopic composition of groundwater

The water input into the river is partly from direct precipitation, but, particularly during dry seasons, the major input is the base flow from groundwater aquifers. Although base flow is ultimately sourced by precipitation, it is useful to know the degree to which its isotopic parameters approximate that of the bulk precipitation.

The stable isotopic composition of groundwater depends on the source of recharge. Because infiltration through the unsaturated zone is usually a non-fractionating process, ground water isotope values are often similar to the mean annual composition of the precipitation, (Gat, 1981; Fritz et al., 1987; Clark and Fritz, 1997; Gonfiantinni et al., 1998). Snowmelt and glacial sources are exceptions as they supply isotopically depleted waters.

The Prairie region could potentially show large stable isotopic differences between precipitation and ground water. While most precipitation occurs in the summer

months, groundwater recharge is primarily due to rain and precipitation in the fall months before the ground freezes and secondarily in the spring months with snowmelt and precipitation infiltrating after the ground thaws. Hence, the groundwater has isotopic characteristics of the cooler spring and fall precipitation (Clark and Fritz, 1997). Such groundwaters may have more negative isotopic values than the local precipitation.

In a semi-arid environment, rivers during the dry season are often at base flow levels, fed by the groundwater system, and this may dominate the isotopic composition of the river itself. In the Canadian Prairies, aquifers are primarily recharged by the spring melt, with large summer rainstorms accounting for only a minimal recharge (McMonagle, 1987). Groundwater $\delta^{18}\text{O}$ values for the Prairie region are approximately -18‰ to -21‰ (Fritz et al., 1987; McMonagle, 1987) and are similar to or more negative than the average $\delta^{18}\text{O}$ of -18‰ for precipitation. This confirms that spring/fall precipitation and later spring runoff are the main sources of the groundwater recharge.

4.3 Discharge flux

Discharge was based primarily on RivDis data (Vörösmarty et al., 1998) and confirmed with the government-controlled database HYDAT (HYDAT, 1998). RivDis data spanned 84 years (1910-1984) for the North Saskatchewan and 83 years (1911-1984) for the South Saskatchewan Rivers. Both sample sets were taken shortly upstream from the confluence, with the North Saskatchewan River sets taken at 53°N -106°W and the South at 52°N -107°W . Annual discharges average $244.2\text{ m}^3/\text{sec}$ ($7.7\text{ km}^3/\text{a}$ total) and $263.9\text{ m}^3/\text{sec}$ ($8.8\text{ km}^3/\text{a}$ total) for the North and South Saskatchewan Rivers, respectively. Seasonally, the highest flow volumes for both rivers are in the summer months, July having $578.1\text{ m}^3/\text{sec}$ in the North and June $657.8\text{ m}^3/\text{sec}$ in the South Saskatchewan River. The lowest flow volume occurs in January in the North Saskatchewan River, with only $52.6\text{ m}^3/\text{sec}$, and in February in the South Saskatchewan River, with $125.2\text{ m}^3/\text{sec}$ (see Figure 9).

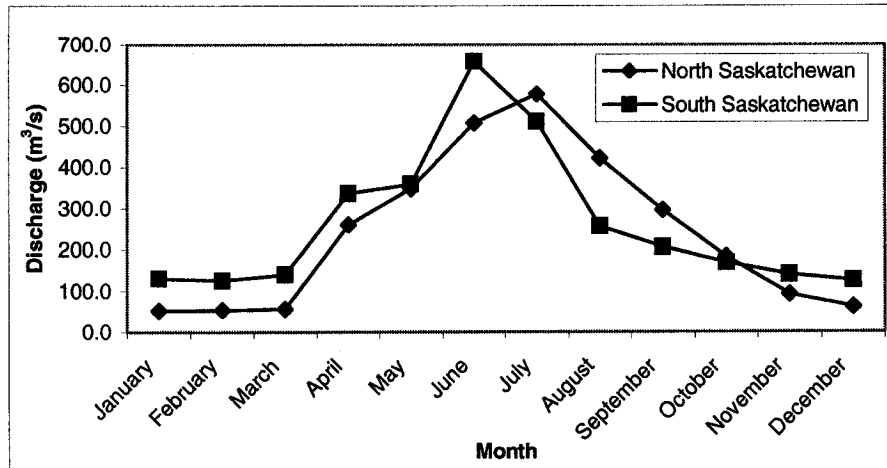


Figure 9: Average monthly discharge in both basins.

4.3.1 Stable isotopic composition of river discharge

Water samples for stable isotopic measurements were collected at the mouth of the North and South Saskatchewan Rivers over a period of one year. In contrast to precipitation data (Figure 7), the $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ of the river water samples showed less seasonal spread (Figure 10). The more depleted values were more ubiquitous during the cooler season. The non-weighted annual average $\delta^{18}\text{O}$ and δD values for precipitation were -18.0‰ and -139‰ , respectively. Weighted precipitation was not used as there were no volume measurements to accompany all of the isotopic measurements. The average $\delta^{18}\text{O}$ for the North Saskatchewan River (-18.7‰) is similar to that for average precipitation (-18.0‰) as well as to groundwater values (-18‰ to -21‰). These similarities suggest that there is little outside influence (i.e. rock/soil interaction) on the isotopic composition of the precipitation as it passes through the ground, becoming part of the groundwater supply and ultimately of the river flux. Evaporative effects, if any, are small. The South Saskatchewan River waters are less negative in ^{18}O and D (Figure 10, 11a), likely a reflection of the location of this basin in a somewhat more southerly, warmer climate.

The least square fit lines generated for the river water samples (Figure 11b) give equations of $\delta\text{D}=5.63*\delta^{18}\text{O}-42.96$ and $\delta\text{D}=4.39*\delta^{18}\text{O}-60.55$ for the North and the South

Saskatchewan watersheds, respectively. Compared to the LMWL for precipitation generated from Edmonton, Saskatoon and Wynyard, both lines show significantly shallower slopes and smaller intercepts (Figure 11b). Their slopes are between four and seven, indicative of water undergoing significant evaporation (Ingraham, 1998). Interestingly, Esther, lying in the middle of the basins, has a MWL of $\delta D = 4.24 * \delta^{18}O - 70.22$ (CNIP, 2001), very similar to the river water line, but distinct from that of precipitation. It is unknown why the Esther data shows such a close similarity to the river data while the data from Saskatoon, closer to the sampling sites, differs. The number of samples may explain this. Edmonton, Wynyard and Saskatoon have five, eight and ten years worth of data while Esther only has two years of sporadic measurements. An alternative, or more likely complementary, explanation may be the secondary evaporation of raindrops before they reach the ground. This can result in precipitation enriched in ^{18}O , relative to precipitation events in other parts of the basins. Finally, the highly negative intercept of the river lines may also indicate the presence of small kinetic effects during evaporation (Ingraham, 1998).

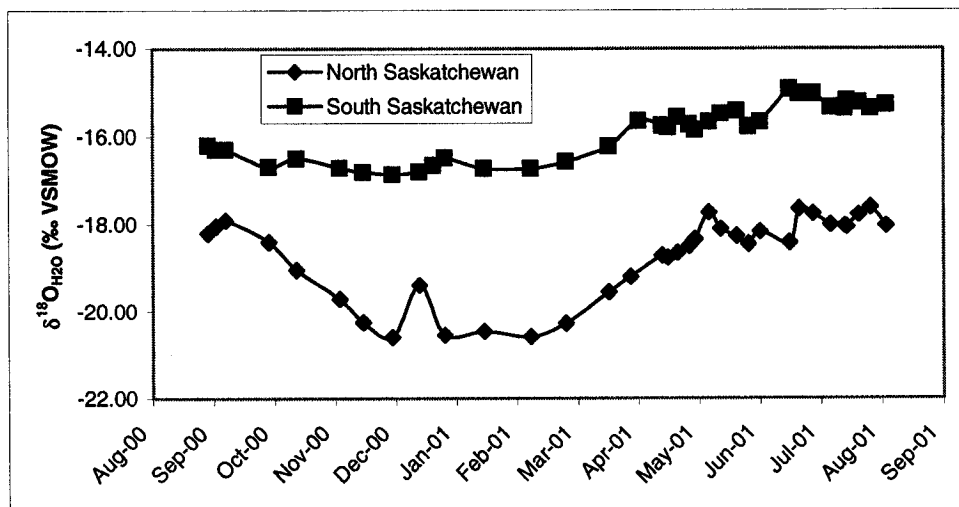


Figure 10: $\delta^{18}O_{H2O}$ in the North and South Saskatchewan Rivers.

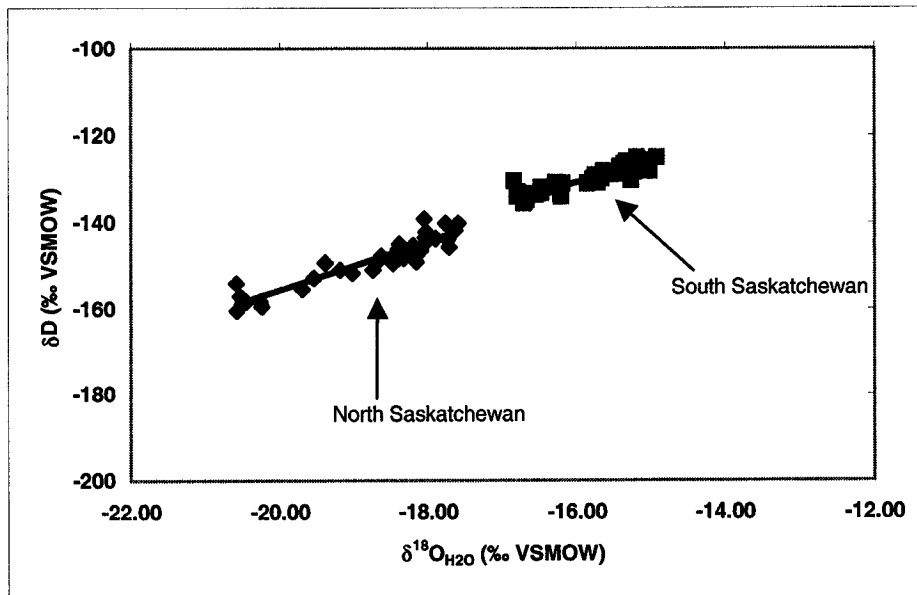


Figure 11: a) Isotope data for river water taken from September 2000 until August 2001.

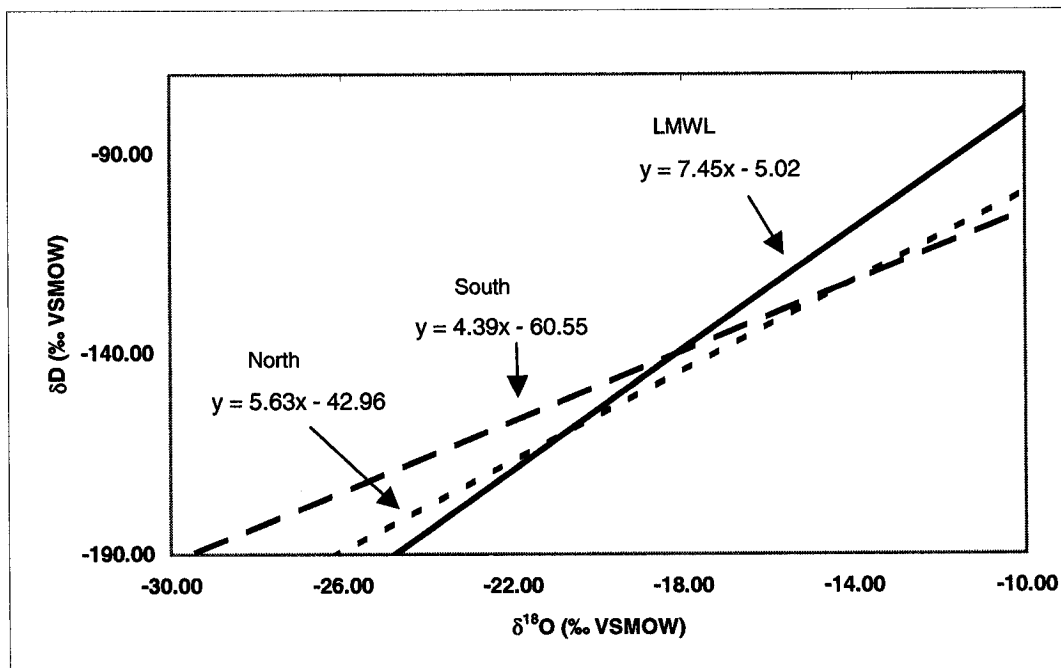


Figure 11: b) The calculated least square linear fits of $\delta\text{D}/\delta^{18}\text{O}$ for the North and South Saskatchewan Rivers compared to the average LMWL from the three primary precipitation stations (Figures 6 and 7).

4.4 Evaporation flux

Evaporation is one of the most difficult components to elucidate as the calculation carries a large uncertainty (addressed later in this study) and most methods devised to estimate evaporation were designed for lakes and standing water bodies. This study uses the approach of Gonfiantini (1986) that, in its various versions, has been implemented for several water balance studies (e.g. Zuber, 1983; Gat and Bowser, 1991; Gat and Matsui, 1991; Gibson et al., 1993).

Evaporation is highly dependent on the relative humidity and temperature of the local air mass. Evaporation takes place when humidity is less than 100% and the vapour pressure of liquid water at its air-water interface is greater than the vapour pressure in the atmosphere (Black, 1991; Brooks et al., 1997). Evaporation can be determined through a complex equation used by Gonfiantini (1986), Gat and Bowser (1991), Gat and Matsui (1991) and Gibson et al. (1993). It should be noted that all variables that are normally expressed in permil must be incorporated into the equation as their actual (ratio decimal) values and not in their permil forms. For example, 10.11‰ would be 0.01011.

The fundamental evaporative equation is based on the work done on free-surface evaporation by Craig and Gordon (1965) in which they stated that:

$$\delta_E = (\delta_S - h\delta_a - \epsilon)/(1-h) \quad (6)$$

and

$$\epsilon = \epsilon^* + \epsilon_k \quad (7)$$

where δ_E is the $\delta^{18}\text{O}$ or the δD of evaporated water, δ_S is the mean water $\delta^{18}\text{O}$ (or δD), in our case the value measured at the mouth of the river, h is the relative humidity given as a fraction, δ_a is the isotopic composition of the $\delta^{18}\text{O}$ (or δD) of the atmospheric vapour, ϵ is the isotopic separation of the liquid and water vapour, ϵ^* is the equilibrium separation factor and ϵ_k is the kinetic separation factor. Using this for a model basis, Gonfiantini (1986) proposed that:

$$x = E/I = [(\delta_S - \delta_1)(1 - h + \Delta\varepsilon)] / [(\delta_S + 1)(\Delta\varepsilon + (\varepsilon/\alpha)) + h(\delta_a - \delta_S)] \quad (8)$$

with

$$\Delta\varepsilon = C_k(1-h) \quad (9)$$

x is the ratio of evaporation to input (here as precipitation). δ_1 represents the mean weighted isotopic composition ($\delta^{18}\text{O}$ or δD) of the precipitation that is based on the intersection of the least square fit line (for the water samples from the mouth of the river), with the local meteoric water line (LMWL) for the region (Figure 11b). The intersection of these lines provides only an approximate estimate to the actual isotopic composition of the precipitation (Gibson et al., 1993). $\Delta\varepsilon$ represents the kinetic enrichment factor for oxygen (or hydrogen) and corresponds to the isotopic enrichment that occurs when water vapour is transported across the air/water interface. C_k expresses the non-equilibrium fractionation of the water at the air/water interface and equals 14.2 and 12.5 for oxygen and deuterium, respectively (Gonfiantinni, 1986). Alternatively, it is 15 and 13 (Merlivat, 1978) and 14.3 and 12.5 (Gibson et al., 1993). These discrepancies in C_k have little effect on the outcome. ε is the enrichment factor (where $\varepsilon = \alpha - 1$) and α is the equilibrium fractionation factor of liquid water for oxygen (or deuterium). α is calculated according to the mean temperature (T) measured in Kelvin and takes the form of $\ln\alpha = AT^{-2} + BT^{-1} + C$ where the values for A , B and C are taken from Majoube (1971), resulting in the equations

$$\ln\alpha = 1137 T^{-2} - 0.04156 T^{-1} - 0.00207 \quad (10)$$

for oxygen and

$$\ln\alpha = 24844 T^{-2} - 76.248 T^{-1} + 0.05261 \quad (11)$$

for hydrogen.

The term δ_a is very difficult to calculate accurately and often carries a large error. There are methods, such as those of Gibson and Edwards (1999), which help obtain a more accurate value for δ_a . The drawback is that these methods are very time intensive and difficult to perform over a long interval. Instead, easier methods are often employed. Frequently, δ_a is estimated based on the basin's proximity to its source of precipitation, usually an ocean or a large sea, and by its distance inland. For example, Gonfiantinni (1986) estimated δ_a from the distance to the sea. It becomes possible to calculate δ_a if one assumes that atmospheric moisture is in equilibrium with local precipitation. Therefore, $\delta_a = \delta_l - \epsilon$ (Gibson et al., 1993).

Gibson et al. (1993) use systematics similar to the one above, with evaporation estimates based on the free-surface evaporation equation of Craig and Gordon (1965). Utilizing the background research of Gat and Levy (1978), their equation produces results similar to those of Gonfiantinni (1986). Gibson et al.'s (1993) equation shows that

$$x = E/I = (\delta_s - \delta_l) / [(h/1-h)(\delta^* - \delta_s)] \quad (12)$$

where $\delta^* = (h\delta_a + \epsilon) / (h - \epsilon)$ and indicates a limiting isotopic enrichment based on the local hydrometric conditions, $\epsilon = \epsilon^* + \epsilon_k$ (similar to that described above) where $\epsilon^* = (\alpha - 1)(1000)$ and $\epsilon_k = C_k(1-h)$. All other variables are the same as those defined previously.

Evaporation calculated using the equations from Gonfiantinni (1986) and Gibson et al. (1993) only show minor discrepancies that relate to derivation of the equations.

δ_s was determined by averaging the $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ of the river samples, giving values of -0.0187 and -0.0159 for the North and South Saskatchewan Rivers. δ_l was determined by locating the intersection between the LMWL (Figure 11b) and the samples' water lines for the North and South Saskatchewan Rivers, resulting in -0.0209 and -0.0183 , respectively. α was calculated using equation (10) and an average temperature of 274.85 and 276.55 K, resulting in 1.01154 and 1.01136 for the North and South Saskatchewan Rivers. ϵ_k values were calculated using average humidity values of 0.71 and 0.65 for the North and South Saskatchewan and the C_k values for ^{18}O . δ_a equated to -0.0324 and -0.0297 for the North and South Saskatchewan, respectively.

M	North Saskatchewan	South Saskatchewan
δ_s	-0.0187	-0.0159
δ_i	-0.0209	-0.0183
δ_a	-0.03244	-0.02967
α	1.011535	1.011358
ϵ	0.011535	0.011358
$\Delta\epsilon$	0.004118	0.00497
H	0.71	0.65
T	274.85	276.55
Evaporation	0.1160	0.1215

Table 1: Variables used in calculating percent evaporation.

Based on calculations performed using equations (8) through (10) for the North Saskatchewan River:

$$\ln\alpha = 1137 (274.85)^{-2} - 0.04156 (274.85)^{-1} - 0.00207 \quad \text{and}$$

$$\Delta\epsilon = 14.2 (1 - 0.71)$$

so

$$x = E/I = [((-0.0187) - (-0.0209))(1 - 0.71 + 0.004118)] / [(-0.0187 + 1)(0.004118 + (0.011535/1.011535)) + 0.71((-0.03244) - (-0.0187))] = 0.116$$

resulting in a total evaporative flux of 5.85 km³/a (11.6%). Using the same equations for the South Saskatchewan River results in:

$$\ln\alpha = 1137 (276.55)^{-2} - 0.04156 (276.55)^{-1} - 0.00207 \quad \text{and}$$

$$\Delta\epsilon = 14.2 (1 - 0.65)$$

so

$$x = E/I = [((-0.0159 - (-0.0183))(1 - 0.65 + 0.00497)] / [(-0.0159 + 1)(0.00497 + (0.011358/1.011358)) + 0.65((-0.02967) - (-0.0159))] = 0.122$$

with the South Saskatchewan River showing a total evaporative flux of 7.56 km³/a (12.2%).

4.5 Interception flux

Interception values were calculated utilizing the leaf types and surface areas found in the North America Land Cover Characteristics Database Version 2.0 (Appendix 1). The Running Vegetation Life form's legend was divided into 7 categories based on leaf types. The databases were then merged into three leaf types: broadleaf, needle leaf and grassland (Figure 12). Heatherington (1987 and references therein) proposed that broad leaf foliage intercepts 14-57%, needle leaf 8-21% and grasslands 5-14% of the gross annual precipitation. Mean interception values of 15% for broad leaf, 36% for needle leaf and 10% for grasslands are utilized in the subsequent calculations. Note, nevertheless, that the grasses in south-western Saskatchewan have been found to intercept up to 21-32% in the growing season (Couturier and Ripley, 1973), two to three times more than the annual averages. Vegetation cover in the North Saskatchewan Basin is divided into 20.2% needle leaf, 38.4% broad leaf and 33.6% grasslands. The vegetation cover in the South Saskatchewan River was comprised of 13.2% needle leaf, 56.3% broad leaf and 25.6% grassland (Figure 12; Table 2).

Multiplying these percentages by the appropriate interception values for each leaf type results in 8.63 km³ (16.4% of precipitation) intercepted in the North Saskatchewan Basin and 9.77 km³ (15.8%) in the South Saskatchewan Basin (Table 2).

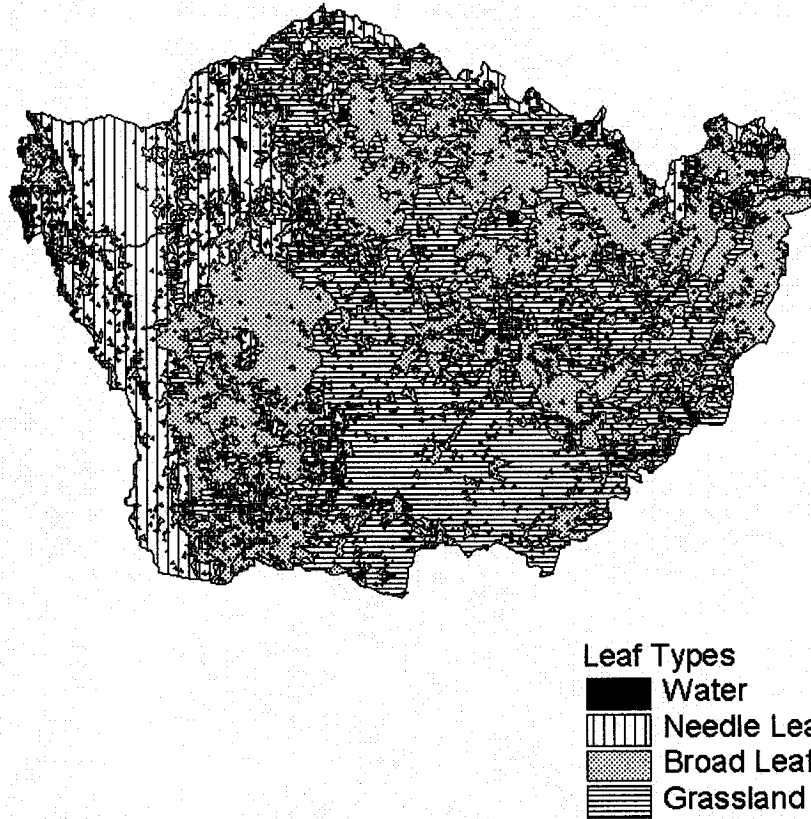


Figure 12: Regional leaf type distributions in the North and South Saskatchewan River watersheds.

Vegetation Type	North Saskatchewan		South Saskatchewan		Combined	
	Area (%)	Intercepted Precipitation (%)	Area (%)	Intercepted Precipitation (%)	Area (%)	Intercepted Precipitation (%)
Needle leaf	20.2	7.3	13.2	4.8	16.7	6.1
Broad leaf	38.4	5.7	56.3	8.4	47.4	7.1
Grassland	33.6	3.4	25.6	2.6	29.6	3.0
Total	92.2	16.4	95.1	15.8	93.7	16.2

Table 2: Aerial distribution (in %) of the leaf types and their average interception values. The total interception is based on the average interception for each basin.

4.6 Transpiration flux

As previously noted, transpiration cannot be effectively measured directly and has to be calculated by difference. Only after the terms in equation (4) and (5) are known can transpiration be determined by the equation:

$$T = ET - E - I \quad (13)$$

where $E = x \cdot P$ and represents the percentage of precipitation that is evaporated in km^3/a . I is the interception value (km^3/a). Transpiration is commonly given as a volume but can easily be changed from a volume into a weight by equating 1 cm^3 to 1 gram of water (or 1 km^3 to 1 Pg).

For the North Saskatchewan River watershed, evapotranspiration accounts for $44.9 \text{ km}^3/\text{a}$ (85.3% of precipitation), evaporation $5.85 \text{ km}^3/\text{a}$ (11.6%) and interception $8.63 \text{ km}^3/\text{a}$ (16.4%). The South Saskatchewan River watershed has evapotranspiration of $53.2 \text{ km}^3/\text{a}$ (85.8%), evaporation $7.56 \text{ km}^3/\text{a}$ (12.2%) and interception $9.77 \text{ km}^3/\text{a}$ (15.8%). Overall, these calculations result in transpiration values of $30.4 \text{ km}^3/\text{a}$ (58.1%) and $35.8 \text{ km}^3/\text{a}$ (57.8%) for the North and South Saskatchewan River, respectively.

4.7 Summary of water balance estimates

The hydrological balances calculations for the watersheds show the primary volume changes and water fluxes within the basins. In the North Saskatchewan Basin, annual precipitation, averaged over 60 years, from 1920-1980 (Legates and Wilmott, 1990) is 52.63 km^3 . Of that amount, 7.73 km^3 (or 14.7%) is discharged at the confluence into the Saskatchewan River system, leaving 44.90 km^3 (85.3%) to be accounted for by evapotranspiration from the basin. Annual interception accounted for 8.63 km^3 (16.4%) of the total basin water flux, while annual evaporation, determined from equations (8, 9), amounted to 5.85 km^3 (11.6%) of the flux. The residual term, transpiration, accounts therefore for the largest portion of the efflux, 30.42 km^3 (58.1%), supporting the dominant role of plant activity on the water fluxes in the basin (Table 3).

In the South Saskatchewan Basin, 60 year records yield mean annual precipitation of 61.98 km³ (Legates and Wilmott, 1990). Of this, 8.83 km³ (14.2%) was discharged into the Saskatchewan River, leaving 53.15 km³ (85.8%) to be accounted for by evapotranspiration. Annual interception amounted to 9.77 km³ (15.8%) and annual evaporation to 7.56 km³ (12.2%) of the annual balance. Annual transpiration once again accounts for the majority of the efflux with 35.85 km³ (57.8%).

	North Saskatchewan		South Saskatchewan	
	km ³ /a	%	km ³ /a	%
Precipitation	52.6	100	62.0	100
Discharge	7.7	14.7	8.8	14.2
Evapotranspiration	44.9 ¹	85.3 ²	53.1 ¹	85.8 ²
Evaporation	5.8 ³	11.6 ⁴	7.6 ³	12.2 ⁴
Transpiration	30.4 ⁵	58.1 ⁶	35.8 ⁵	57.8 ⁶
Interception	8.6 ⁷	16.4	9.8 ⁷	15.8

- 1: **Evapotranspiration = Precipitation - Discharge**
- 2: **Evapotranspiration % = Evapotranspiration/Precipitation x 100**
- 3: **Evaporation = Evapotranspiration - Transpiration - Interception**
- 4: **Evaporation % = Evaporation/Precipitation x 100**
- 5: **Transpiration = Evapotranspiration - Evaporation - Interception**
- 6: **Transpiration % = Transpiration/Precipitation x 100**
- 7: **Interception = Precipitation x Intercepted %**

Table 3: North and South Saskatchewan Basin water balances. Precipitation was averaged over 60 years and discharge was averaged over 30 years. All other variables were calculated according to the method outlined.

Chapter 5

TERRESTRIAL PHOTOSYNTHESIS/RESPIRATION BALANCE OF THE WATERSHEDS

A watershed can be partitioned into the terrestrial and aquatic ecosystems. Terrestrial plants gain carbon while simultaneously losing water to the atmosphere at a predetermined ratio called the Water Use Efficiency (WUE). This relationship enables a quantitative consideration of the role that terrestrial plants play in controlling the carbon content of the watershed.

5.1 Terrestrial water utilization efficiency

Water use efficiency (WUE) is a measure of a plant's ability to photosynthesize carbon while simultaneously losing water to the atmosphere at a ratio of 1 molecule of CO₂ to almost 1000 molecules of water. WUE is therefore a variable essential for calculation of the photosynthetic flux of carbon from transpiration data. WUE is based on the plant type and its photosynthetic pathway. Plants can be divided into two major types characterized by their photosynthetic pathways and are designated C₃ and C₄. The North and South Saskatchewan Basin land covers were divided into C₃ and C₄ using the North American Seasonal Land Cover Legend as a basis. The Simple Biosphere Model's legend was used in conjunction with a vegetation classification legend found in FLUXNET (Appendix 1) to determine whether the vegetation in the Seasonal Land Cover Characteristics legend was C₃ or C₄ in nature. The land cover file was clipped in Arc View according to the watershed boundaries and the associated table was then exported into a spreadsheet and manually correlated with the vegetation list produced through a combination of the Simple Biosphere and FLUXNET legends. When the vegetation was typed, another associated file was created consisting only of C₃ and C₄ classifications, thereby giving their relative percentages in each basin and the average

WUE values (Table 4; Figure 13). Note that C₄ plants comprise only a marginal element of this Prairie biome, although some long grass species are more common in southern prairies.

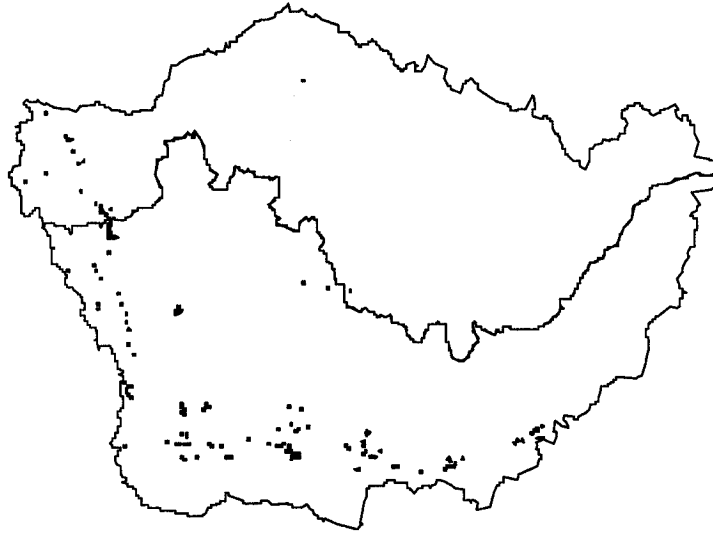


Figure 13: Regional distribution of C₃ and C₄ plant types. C₃ plants dominate both basins, accounting for 97.6% of the vegetation cover and are denoted by the clear portions of the diagram. C₄ distribution comprised 0.4% in the North Saskatchewan and 2.0% in the South Saskatchewan basins and is denoted by the dark colour in the diagram.

Compared to C₃ plants, C₄ plants incorporate an additional pathway when fixing carbon during photosynthesis and, as a result, they are more efficient at using water than C₃ plants. This water use efficiency of plants is nevertheless difficult to ascertain, because it often depends on the plant species, not just the type (Hopkins, 1995; O’Leary, 1988). The daily ‘instantaneous’ WUE’s are characterized by relatively small ratios of 500:1 for C₃ and 250:1 for C₄ plants, respectively (Taiz and Zeiger, 1991). In contrast, longer term WUE’s, considered in years, have a molar ratio of water to carbon of 1000:1 for C₃ and 500:1 for C₄ plants (Schantz and Piemeisel, 1927). These are utilized here for calculating

the overall WUE values for the watersheds. The average WUE for the North, South and combined Saskatchewan Rivers are 998, 990 and 994, respectively (Table 4).

	North Saskatchewan	South Saskatchewan	Combined
C₃ Vegetation (%)	99.6	98.0	98.8
C₄ Vegetation (%)	0.4	2.0	1.2
Water Use Efficiency	998	990	994

Table 4: Distribution of C₃ and C₄ vegetation and their average water use efficiency.

5.2 Terrestrial net primary productivity

Net primary productivity (NPP) is defined as the amount of new plant tissue created over a given area over a specified period of time or the total photosynthetic gain minus the respiratory losses of vegetation per unit surface area. NPP is calculated from transpiration estimates using the WUE for a given area and ecosystem. Transpiration may be determined by equation (13) while the WUE is dependent on the photosynthetic pathway used by C₃ and C₄ plants. Calculation of WUE and C₃ and C₄ plants is covered in a preceding section. NPP can be mathematically defined as:

$$\text{NPP (moles C/a)} = \text{Transpiration (moles H}_2\text{O/a)} \times \text{WUE (moles C/moles H}_2\text{O)} \quad (14)$$

NPP and NEP (net ecosystem productivity) are two measures of general productivity within a given area, with NPP measuring productivity over years and NEP accounting for productivity over decades. The NEP is the difference between the NPP and the heterotrophic soil carbon release (R_h) and, thereby, always a lesser quantity than the NPP (Buchmann and Schulze, 1999). Additionally, the NEP represents the

ecosystem's carbon loss or gain without accounting for any other carbon affecting disturbances, including forest fires, harvesting and DOC exports (Prentice et al., 2001).

As noted in equation (5), evapotranspiration was partitioned into its evaporation, interception and transpiration components. Utilizing the transpiration estimates, interception values and plant genotypes discussed previously (Figures 12, 13), the North Saskatchewan Basin has a WUE of 998 and the South Saskatchewan Basin 990 (Table 4). From equation (14), with the transpiration of 30.42 km³ and WUE of 998 for the North Saskatchewan basin, the NPP is as follows:

$$\begin{aligned}
 30.42 \text{ km}^3 &= 30.42 \cdot 10^{15} \text{ grams} \\
 30.42 \cdot 10^{15} \text{ grams} / 18 &= 1.69 \cdot 10^{12} \text{ moles water} \\
 1.69 \cdot 10^{12} \text{ moles water} / 998 &= 1.69 \cdot 10^{12} \text{ moles carbon} \\
 1.69 \cdot 10^{12} \text{ moles carbon} \cdot 12 &= 2.03 \cdot 10^{13} \text{ grams carbon} = 0.0203 \cdot 10^{15} \text{ grams carbon} \\
 \text{NPP} &= 0.0203 \cdot 10^{15} \text{ grams carbon}
 \end{aligned}$$

For the South Saskatchewan, with transpiration of 35.85 km³ and a WUE of 990:

$$\begin{aligned}
 35.85 \cdot 10^{15} \text{ grams} / 18 &= 1.99 \cdot 10^{15} \text{ moles water} \\
 1.99 \cdot 10^{15} \text{ moles water} / 990 &= 2.01 \cdot 10^{12} \text{ moles carbon} \\
 2.01 \cdot 10^{12} \text{ moles carbon} \cdot 12 &= 2.41 \cdot 10^{13} \text{ grams carbon} = 0.0241 \cdot 10^{15} \text{ grams carbon} \\
 \text{NPP} &= 0.0241 \cdot 10^{15} \text{ grams carbon}
 \end{aligned}$$

The North and South Saskatchewan Basins cumulatively take up $4.44 \cdot 10^{13}$ g C (or 0.0444 Pg C) annually. With the cumulative area of 267,100 km², this equates to a spatial average NPP of 166.0 g C/m²/a (166.1 g C/m²/a and 165.9 g C/m²/a for the North and South Saskatchewan Basins, respectively).

NPP, temperature and precipitation values for the North and South Saskatchewan River basins lie along the edge of the grasslands ecosystems, close to the Boreal forest ecosystems (Figures 14, 15). By comparison, the same parameters for the Ottawa River watershed (Telmer and Veizer, 2000, 2001), a predominantly cool temperature ecosystem, plot nearly at the edges of the boreal, temperate and grassland domains. The

average yearly precipitation in the Ottawa watershed is twice that of the North and South Saskatchewan watersheds, while the average yearly temperature is only slightly higher. The resulting NPP for the Ottawa River basin exceeds that of the Saskatchewan watersheds, at $\sim 200 \text{ g C/m}^2/\text{a}$ versus $\sim 166 \text{ g C/m}^2/\text{a}$, reflecting the Ottawa River basin's forested nature. Nevertheless, they both fall into the general trend of NPP dependency on precipitation, a feature evident from Figure 15.

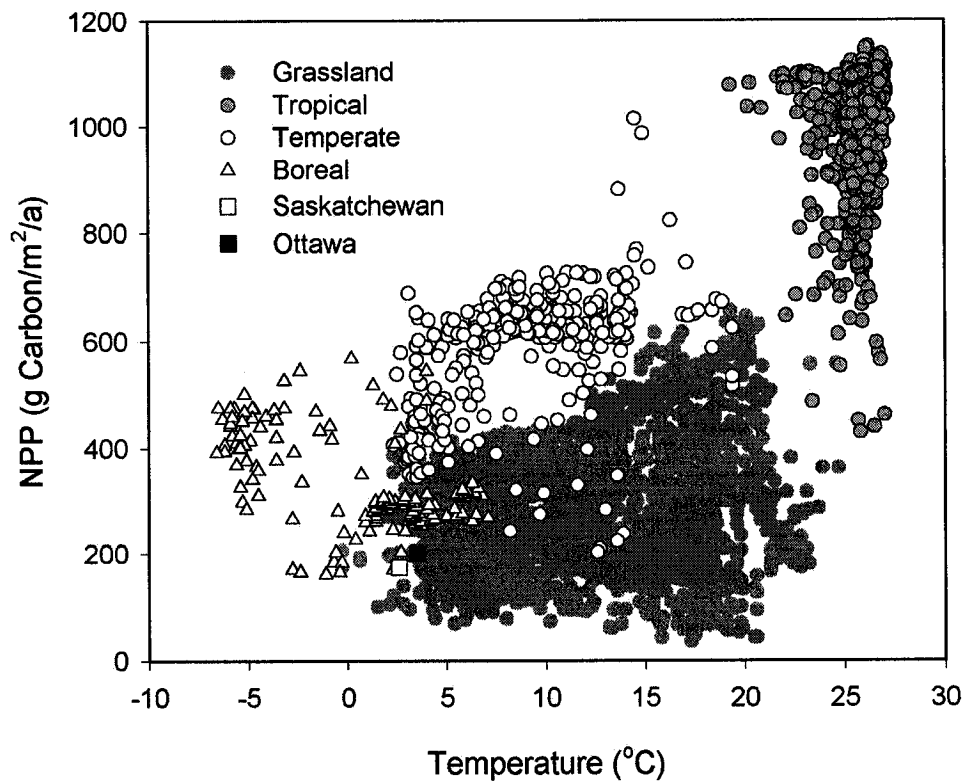


Figure 14: NPP data plotted against temperature. Further explanations as in Figure 1.

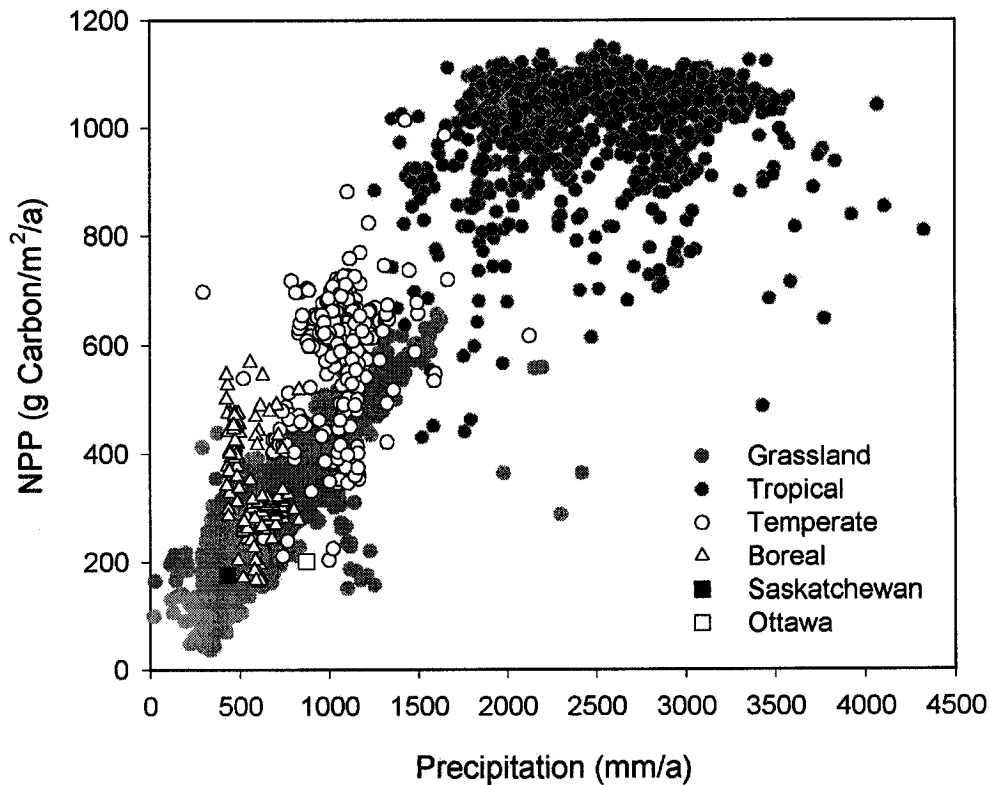


Figure 15: NPP data plotted against precipitation. Further explanations as in Figure 1.

5.3 Terrestrial carbon source or sink?

In order to establish whether the North and South Saskatchewan watersheds are a net source or sink of CO₂, it is essential to compare the above estimates of NPP with respiration fluxes or, in other words, to estimate the Net Ecosystem Productivity (NEP)

$$NEP \text{ (g C/a)} = NPP \text{ (g C/a)} - R_h \text{ (g C/a)} \quad (15)$$

where R_h is the heterotrophic soil respiration. Heterotrophic soil respiration is the difference between the total soil respiration and the autotrophic (root) respiration.

Soil respiration is the primary mechanism for plants of returning CO₂ to the atmosphere and is considered to be one of the largest global carbon fluxes (Schlesinger and Andrews, 2000). Complete soil respiration is due primarily to decay of organic matter in the soil, root respiration by plants and respiration by bacteria within the soil horizons. Soil CO₂ emissions can be divided into two components: the heterotrophic component, which includes microbes and decaying organic matter, and the autotrophic component, which is the root system of plants (Hanson et al., 2000; Rochette et al., 1999). The majority of the CO₂ released from the soil is autotrophic in nature. It is therefore imperative that the soil CO₂ emissions be partitioned into their heterotrophic and autotrophic components. Many studies attempted to partition the soil CO₂ emissions and included such methods as the isotopic mass balance of carbon (Rochette et al., 1999), root exclusion, component integrations and trenching (reviewed in Hanson et al., 2000). Results from these techniques vary, but they all concluded that forested regions have higher values associated with autotrophic respiration than their non-forested counterparts. Root depth, temperature and ground cover are a few of the causes for these higher values. For instance, large woody plants (trees) have larger, deeper rooting systems while shrubs and grasses have much shallower, more confined roots, and forested regions have more litter while non-forested areas are more exposed.

Estimates of the autotrophic component of the soil CO₂ flux range from 30-65%, depending on the age of the stand, with the heterotrophic flux ranging from <20% to >60% in non-forested regions (Hanson et al., 2000). By taking mean values, Hanson et al. (2000) estimated that non-forested regions had 46% contributions from root respiration while forested regions had a 60% contribution.

	North Saskatchewan	South Saskatchewan	Combined
Forested %	21	31	26
Non-forested %	79	69	74
R_n (Pg C/a)	0.0204	0.0266	0.024

Table 5: Land cover of the North and South Saskatchewan basins.

The North and South Saskatchewan basins were divided into forested and non-forested areas (Table 5) using the North America Land Cover Database Version 2.0 (Appendix 1). Then, by taking the total soil CO₂ emission data provided by Raich and Potter (1995) (386.9 and 416.3 g C/m²/a for the North and South Saskatchewan areas, respectively) and subtracting the amount of CO₂ provided by autotrophic respiration calculated using percentages from Hanson et al. (2000), values of 166.2 g C/m²/a for the North and 184.6 g C/m²/a for the South Saskatchewan watersheds were determined to represent the heterotrophic components.

Annual heterotrophic soil respiration values are 2.04×10^{13} , 2.66×10^{13} and 4.7×10^{13} g C for the North, South and combined Saskatchewan basins (Table 6). Considering the uncertainties involved in calculating these parameters, the deviations from the NPP estimates are so minor that the ecosystems can be considered in effective equilibrium. Richey et al. (2002) made a similar observation for the Amazon River basin and Lee and Veizer (in press) for the Mississippi system and its sub-basins.

	North Saskatchewan	South Saskatchewan	Total
Transpiration (km³ H₂O)	30.4	35.8	66.2
NPP (Pg C)	0.020	0.024	0.044
NPP (g C/m²)	166	185	351
Heterotrophic Soil Respiration (Pg C)	0.020	0.027	0.047
NPP/ Heterotrophic Soil Respiration	1	0.91	0.96

Table 6: Annual NPP and soil respiration fluxes.

By comparison, the Ottawa River basin does not necessarily show equilibrium between carbon sequestration and release. Using transpiration, WUE and plant type data from Telmer and Veizer (2000), the annual NPP for the Ottawa River watershed equals 4.0×10^{13} g C. Soil respiration values were calculated from the same database as for the North and South Saskatchewan basins, and were clipped for the Ottawa's basin boundaries. Because the land cover was unknown, forest covers of 50 and 100% were used in order to constrain the possible root respiration values. Based on this data, the 50 and 100% forest cover gave annual heterotrophic respiration values of 3.32×10^{13} and

2.82×10^{13} g C, respectively. With the annual NPP of 4.0×10^{13} g C, the heavily forested Ottawa River basin appears to be a moderate carbon sink.

5.4 Uncertainties and Error Propagation

It must be stated that the above estimates of carbon fluxes are order of magnitude approximations because the possible errors are large. The hydrological budgets of the basins are relatively well constrained given the time period which they encapsulate. Time coverage of thirty or more years would account for any exceptional variations due to extreme weather events, such as flooding or drought, changes in discharge or in precipitation. On the other hand, the complex evaporation calculations, developed by Gonfiantinni (1986) from the free surface evaporation equations of Craig and Gordon (1957), were created for lakes and its application for watersheds may not be entirely straightforward. Similarly, the interception term, based primarily on map interpretations and plant leaf designations, has an uncertainty of $\pm 50\%$ relative to the utilized average values. This alone can result in an uncertainty of $\pm 15\%$ in the transpiration water flux that is calculated as a residual.

The most critical term, however, is the water use efficiency value. WUE values show a large range for each plant genotype. Schantz and Piemeisel (1927) claimed that the long term WUE for C_3 and C_4 plants were 1000 ± 250 and 500 ± 70 , respectively. If so, the inherent uncertainty would be about $\pm 25\%$. It is these values that are transposed into many studies, such as Taiz and Zeiger (1991) and Orsenigo et al. (1997), even though they may not be representative of all the ecosystems, particularly the forest and woody stem ones. Considering that short term WUE's are about one half of the long term ones, the intermediate WUE's may be a more realistic reflection of a real situation. If so this would increase the calculated NPP values. We therefore cannot entirely discount the possibility that the Saskatchewan Prairie ecosystems are potentially CO_2 sinks. Nevertheless, the agreement between our NPP and the literature respiration data is intriguing, suggesting as a minimum that the water balance approach is a viable alternative.

5.5 Summary of terrestrial photosynthesis/respiration fluxes

The water balance evaluation of the Saskatchewan watersheds shows that the total precipitation is 52.63 and 61.98 km³ for the North and South Saskatchewan basins, respectively. From this total supply, transpiration accounts for 30.42 and 35.85 km³ for the North and South Saskatchewan watersheds, respectively. Transpiration thus accounts for just over 57% of the water loss from both basins. Combined with WUE, it results in annual NPP values of 2.03×10^{13} g C/a (or 166.1 g C/m²/a) and 2.41×10^{13} g C/a (or 165.9 g C/m²/a) for the North and South Saskatchewan basins, respectively. Heterotrophic soil respiration values for the North and South Saskatchewan are 2.04×10^{13} and 2.66×10^{13} g C, respectively, suggesting that photosynthesis/respiration fluxes in the basins are in equilibrium.

Chapter 6

AQUATIC PHOTOSYNTHESIS/RESPIRATION BALANCE OF THE RIVERS

A watershed may be divided into two principal components: the terrestrial and aquatic. The terrestrial portion was dealt with in Chapter 5. The focus of the second half will be on the aquatic/riverine aspect of the watershed.

The NPP calculations in Chapter 5 account for the entire basin, but in reality reflect only the terrestrial portion of the watershed. Aquatic plants utilize river water for photosynthesis. This component was previously included in the discharge portion of the hydrological budget. The photosynthesis/respiration balance of a river indicates the flux of carbon in the *aquatic* portion only.

6.1 Chemical and isotopic composition of the rivers

The chemistry of river water helps to constrain variables such as dissolved gas concentrations, temperature, pH, ion concentration and general water quality. Such knowledge is essential to understand the processes controlling the biological activity, hence the R:P balance of the system.

6.1.1 Total dissolved solids (TDS)

TDS is a measurement of the solids dissolved in the water. These include salts, metals and most commonly sulphates, bicarbonates and carbonates. The TDS of the North and South Saskatchewan Rivers fall between 150 and 280 mg/L, with the highest value in November (277.6 mg/L) for the North Saskatchewan and May (260.0 mg/L) in the South Saskatchewan River (Figure 16). Rapid decreases in TDS occurred in late March and April as snow and ice melt waters diluted the river waters. TDS then increased and remained steady throughout the rest of the sampling period, averaging, from May to August, 183 and 244 mg/L for the North and South Saskatchewan Rivers,

respectively. Minor fluctuations resulted from increasing inputs from precipitation throughout the summer months.

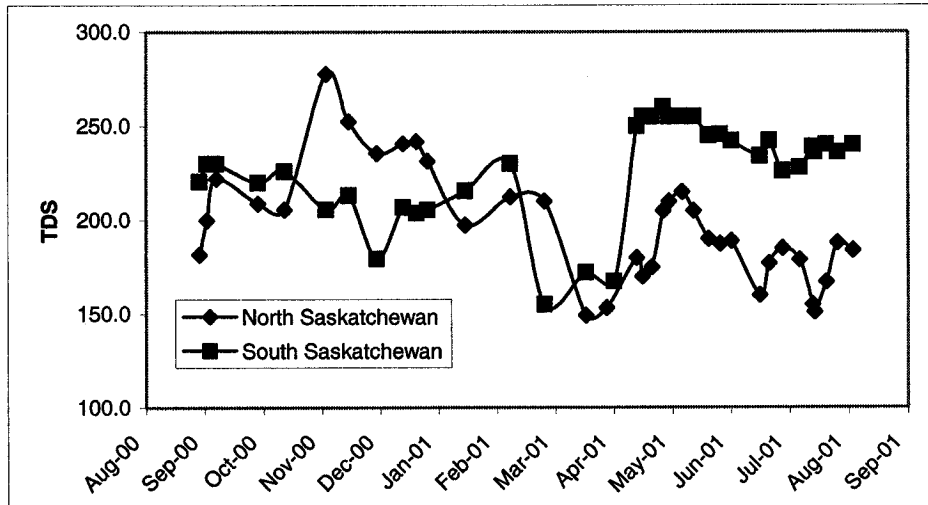


Figure 16: TDS in the North and South Saskatchewan Rivers.

6.1.2 Alkalinity, pH, pCO₂

Carbonate alkalinity is a measure of water's ability to neutralize and buffer acids and stabilize pH values. Alkalinity in the North Saskatchewan River showed larger fluctuations than in the South Saskatchewan, ranging from 90 to 260 mg/L in the North Saskatchewan and 90 to 190 mg/L in the South Saskatchewan (Figure 17; Appendix 3), but the actual range of values may be more restricted because the unusually low September measurements do not fit the general pattern. Since these were the first measurements, field analytical technique error cannot be excluded. Generally, both rivers showed their highest alkalinity in the colder months, the North Saskatchewan River in October at 257 mg/L and the South Saskatchewan River in January at 195 mg/L. After the snow and ice melt, both rivers show a marked drop, followed by an increase to relatively steady alkalinity throughout the warmer months, May to August, with averages of 136 and 160 mg/L for the North and South Saskatchewan, respectively. Alkalinity and

TDS are both are strongly associated with the HCO_3^- content in the waters. This is addressed more fully in a subsequent section.

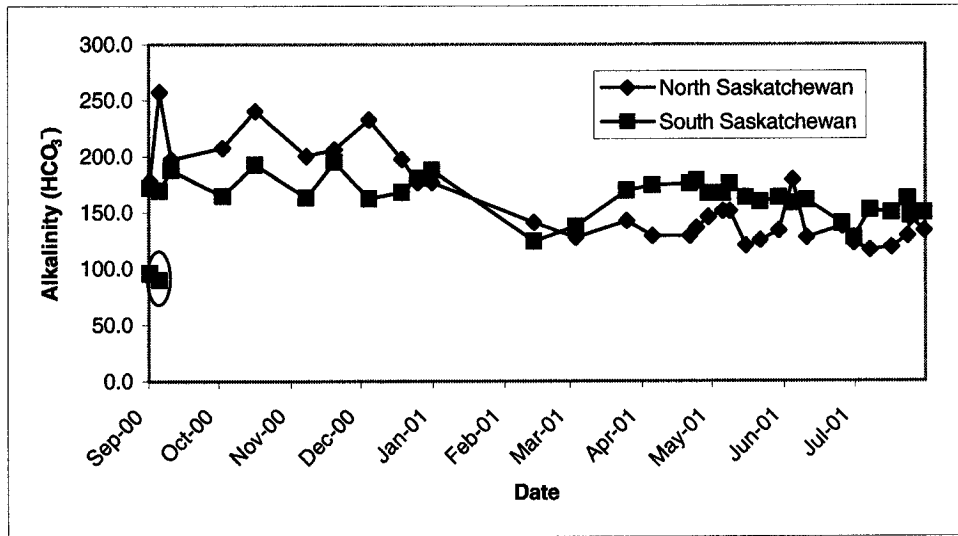


Figure 17: Alkalinity in the North and South Saskatchewan Rivers. Circle indicates samples with likely field analytical errors.

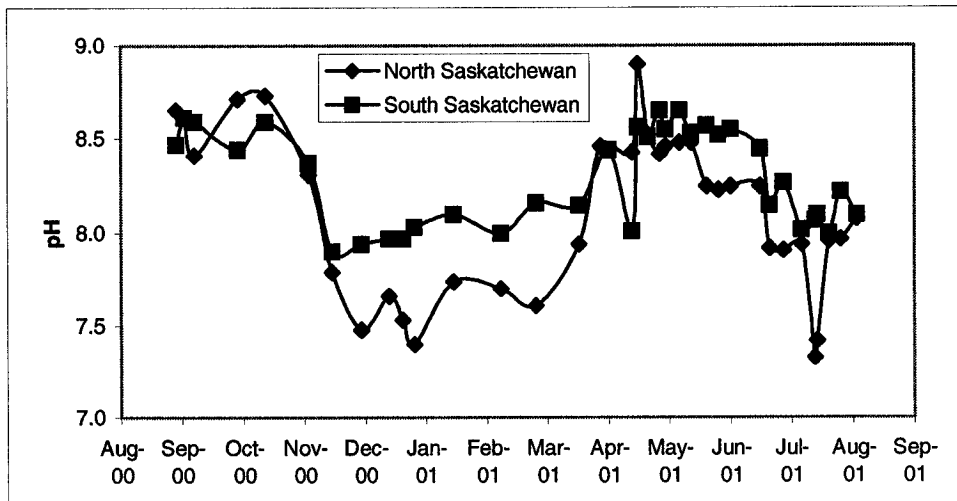


Figure 18: pH in the North and South Saskatchewan Rivers.

As seen in Figure 18, both the North and South Saskatchewan River systems showed similar pH values and fluctuations, although those for the North Saskatchewan were more pronounced. The North Saskatchewan has pH ranging from 7.3 to 8.9 with a

yearly average of 8.1. The drop in pH exhibited shortly after October was attributed to the increased influence of base flow that usually has a lower pH due to the dissolution of soil CO₂ into the groundwater. This lowers the pH to 7.7 on average during the colder months, particularly at times of ice cover across the river, followed a marked increase in the spring and summer, to an average of 8.2. The marked pH drops in August were due to a large storm event. These spikes are associated with the increased sediment load, turbulence and discharge, caused by a disproportionate volume of water being added to the river from the storm.

Partial pressure of carbon dioxide (pCO₂) in the water column results from several processes, including invasion or evasion of CO₂, soil and groundwater input, and photosynthetic/respiratory activities of biota within the water column. The present CO₂ concentration of the atmosphere is ~ 360 ppm (NOAA, 1999).

Unlike alkalinity and pH, the pCO₂ levels are radically different between the two river systems, although the overall trends are somewhat similar (Figure 19). In the North Saskatchewan, pCO₂ values increased from near atmospheric levels in September to extremely supersaturated values from November onward, reaching 3,000 to 6,000 ppm, quantities up to ten to fifteen times normal atmospheric levels. These values coincided with the colder months and with complete ice cover. pCO₂ significantly decreased with the melting of the ice cover, dropping to near atmospheric levels and remaining there until it begins to rise again in June to values in excess of 1,000 ppm. The spike of 5,000-6,000 ppm in August is the result of a storm event, likely due to 'flushing' of groundwaters from the aquifer by the storm water mass.

The South Saskatchewan River, despite a similar, but subdued, temporal pCO₂ pattern shows much lower values in the winter months. When the ice cover was complete, pCO₂ values rose to only three to five times atmospheric concentrations, reaching the maximum in early December, and then decrease until April as the ice cover melts. As for the North Saskatchewan, the pCO₂ remains slightly above atmospheric values from May until mid-July, rising again to five times atmospheric concentrations in the summer (Figure 19).

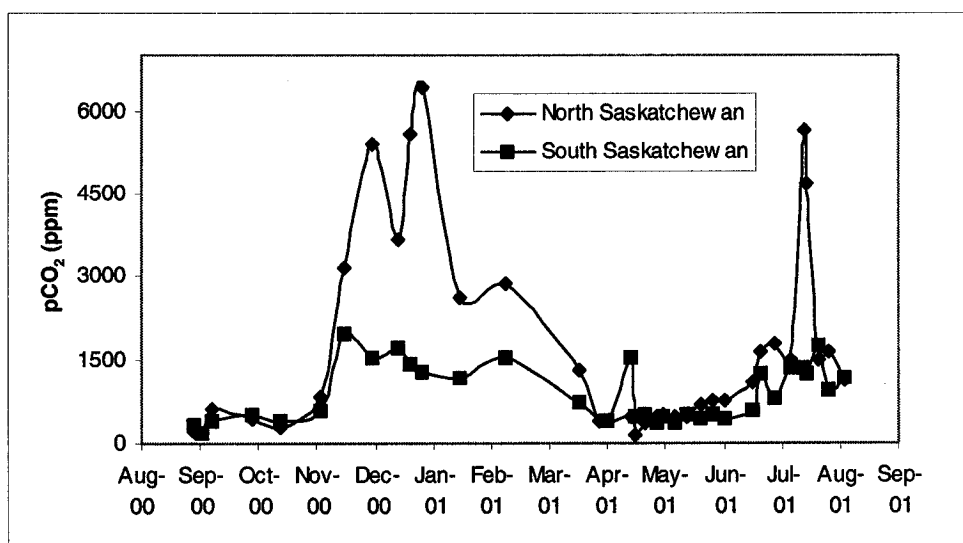


Figure 19: pCO₂ in the North and South Saskatchewan Rivers.

The much lower South Saskatchewan values during the winter season may be due to the lack of complete ice cover at the sampling point. For a period of time, ice cover was not complete and the eastern bank was exposed to atmosphere, particularly in January. Also, the Gardiner dam at Lake Diefenbaker and the Saskatoon weir, 250 km and 100 km upstream from the sampling point, respectively, remain uncovered by ice throughout the colder months, promoting continuous gaseous exchange with the atmosphere. These three reasons may be why the annual average for the North Saskatchewan is twice that of the South, with 1759 ppm versus 885 ppm, in the winter months.

6.1.3 Plants and their $\delta^{13}\text{C}_{\text{org}}$

Generally, terrestrial plants take up CO₂ from the atmosphere through openings in the leaves called stomata. The degree that these stomata open or close depends on the surrounding environment, including light intensity, humidity, temperature and CO₂ concentrations. CO₂ passes through the stomata into the leaf and carbon is incorporated into the plant utilizing one of three photosynthetic pathways: C₃, C₄ and CAM (O'Leary, 1988).

The C₃ pathway uses the Calvin Cycle, which utilizes the carboxylation enzyme RUBISCO to fix carbon (Bowen, 1988; Gillon et al., 1998). C₃ plants dominate much of the present terrestrial ecosystems and consist of grasses, woody plants and many crops. Their main advantage is their ability to flourish in conditions where there are high levels of CO₂ present (Ehleringer et al., 1991). C₃ plants dominate the North and South Saskatchewan basins, accounting for more than 97% of the terrestrial vegetation (Table 4).

C₄ plants use the Hatch-Slack cycle to fix carbon (Bowen, 1988). This mechanism takes advantage of the PEPC carboxylation enzyme to fix CO₂ and is superior to the C₃ pathway in that it more effectively concentrates CO₂ in the leaf. Interestingly, this enzyme can also use the bicarbonate ion as another carbon source (Gillon et al., 1998), actively drawing bicarbonate into its structure. The C₄ pathway is surmised to have developed in response to a significant decrease of carbon dioxide in the Cretaceous and Tertiary (Ehleringer et al., 1997). Because C₄ plants have such an effective CO₂ concentrating mechanism, they thrive in areas of high temperatures and high light intensities with low carbon dioxide concentrations. However, at the present concentrations of 360 ppm in the atmosphere, plants with C₃ photosynthetic pathways are favoured and should flourish even more in the future (Ehleringer et al., 1997). C₄ plants constitute only 2.4% of the terrestrial vegetation in the study area.

CAM plants incorporate pathways similar to C₃ and C₄ plants. The primary difference is that CAM plants utilize the C₃ pathways during daylight hours, when highest productivity occurs, and the C₄ pathway during dark hours. This shift in pathway utilization occurs in response to the plant's malic acid content. As the majority of these consist of desert and succulent plants, no CAM plants are present in the area encompassing the North and South Saskatchewan River systems.

Due to the chemical and physical properties imparted by the mass differences between the isotopes of ¹³C and ¹²C, plants discriminate photosynthetically against the heavier carbon isotope, ¹³C. Plants preferentially uptake ¹²C, thereby enriching the surrounding environment in ¹³C. C₃ and C₄ discrimination produces isotopic signatures that are radically different, with CAM plants falling in between. C₃ plants generally contain less ¹³C than the atmosphere and have an internal ¹²C:¹³C of 91:1 (Farquhar et al.,

1989), producing $\delta^{13}\text{C}$ of -21‰ to -36‰ , with an average of -28‰ (O'Leary, 1988). C_4 plants, on the other hand, have less fractionated $\delta^{13}\text{C}$ of -6‰ to -19‰ , with an average of -14‰ (O'Leary, 1988). CAM plants produce C_{org} with $\delta^{13}\text{C}$ ranging from -10 to -20‰ due to their dual nature. In contrast, respiration does not involve isotope fractionation. As a result, the isotopic composition of the respiratory CO_2 will be similar to that of the source material (O'Leary, 1988).

6.1.4 Dissolved inorganic carbon (DIC) and $\delta^{13}\text{C}_{\text{DIC}}$

When CO_2 dissolves into water, it speciates into four forms: $\text{CO}_{2(\text{aq})}$, H_2CO_3 , HCO_3^- and CO_3^{2-} . The relative concentrations of these species are a function of pH, with pH of 2.0-6.4 generated mainly by $\text{CO}_{2(\text{aq})}$, 6.4-10.3 by HCO_3^- and 10.3-14.0 by CO_3^{2-} (Stumm and Morgan, 1996). Greater amounts of gases can dissolve into colder water and is the case not only for carbon dioxide, but also for oxygen. Atmospheric $\delta^{13}\text{C}$ values presently stand at about -7‰ (Clark and Fritz, 1997), but river waters in equilibrium with such atmospheric CO_2 should have $\delta^{13}\text{C}_{\text{DIC}}$ value of ~ 0 to -1‰ (Figure 20). Since this is usually not the case, the carbon isotopic composition of DIC is controlled by additional factors. These may include:

- 1) carbonate and silicate rock weathering (having $\delta^{13}\text{C}$ from $+1$ to $+2\text{‰}$ for carbonates and -6 to -7‰ for silicates today) (Bowen, 1988);
- 2) equilibration with atmospheric CO_2 ;
- 3) degradation and oxidation of organic material;
- 4) tributary/groundwater/soil water inputs; and
- 5) photosynthetic consumption of CO_2 and its respiratory release by biological organisms within the river (Yang et al., 1996; Clark and Fritz, 1997; Atekwana and Krishnamurthy, 1998; Helie et al., 2002).

The carbon isotopic composition of DIC in river water mirrors the isotopes of the dominant source of carbon although the $\delta^{13}\text{C}_{\text{DIC}}$ may temporarily decrease when the addition of large quantities of water results in dilution (Atekwana and Krishnamurthy,

1998). For instance, the Ottawa River $\delta^{13}\text{C}_{\text{DIC}}$ ranges from -11.3 to -4.1 ‰ (Helie et al., 2002), with an average of -9.0 ‰ (Telmer, 1997). These depleted values are primarily a result of carbonate dissolution by soil CO_2 charged groundwaters. In contrast, the St. Lawrence River has $\delta^{13}\text{C}_{\text{DIC}}$ values ranging from -13.7 to $+2.2$ ‰, with an average of -2.0 ‰ (Barth and Veizer, 1999). These enriched values are produced by enhanced atmospheric exchange, due to the long residence time of the bulk of river water in the Great Lakes, complemented by increased photosynthetic activity in the summer and fall months (Yang et al., 1996).

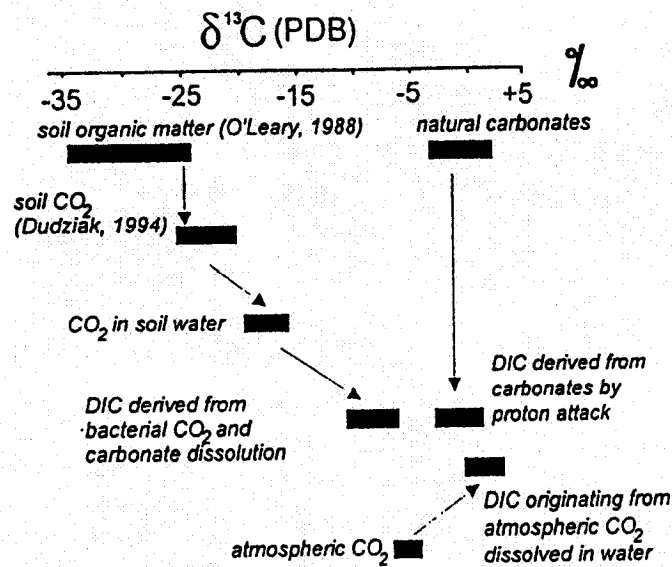


Figure 20: Isotopic composition of carbon in natural systems. Reproduced with permission from Pawellek and Veizer (1994).

Carbonate rocks dominate the geology and the composition of the glacial drift in the North and South Saskatchewan basins. The dissolution of carbonate rocks may shift $\delta^{13}\text{C}_{\text{DIC}}$ towards 0 to -2 ‰, a value typical of Palaeozoic marine limestones (Helie et al., 2002), but carbonate dissolution in the river itself is found to play only a minor role in the generation of DIC (Yang et al., 1996). However, carbonate dissolution has a greater effect on groundwaters that feed river systems.

Soil CO_2 is derived primarily from decomposition of organic matter and the initial isotopic composition of soil CO_2 is dependent on the nature of the organic matter. Soils

dominated by C₃ matter will produce δ¹³C between -24 and -28‰, values similar to C₃ plants (see section 6.1.2). Similarly, soils dominated by C₄ matter will result in δ¹³C of -6 to -19‰ (O’Leary, 1988). Because the dissolution of soil CO₂ into the water results in a fractionation of +7‰, the resulting δ¹³C_{DIC} varies between -17 to -21‰ and +1 to -12‰ for the C₃ and C₄ dominated soils, respectively (Wigley et al., 1978; O’Leary, 1988). As the North and South Saskatchewan basins are dominated by C₃ foliage, the δ¹³C_{DIC} should lie between -17 and -21‰ (Figure 20).

Similar to soil CO₂, the atmospheric CO₂ dissolving into water fractionates by +7‰, producing δ¹³C_{DIC} of about 0‰ (Yang et al., 1996). The impact of atmospheric CO₂ on equilibrium aquatic δ¹³C_{DIC} is possible to calculate (e.g. Zhang et al., 1995; Helie et al., 2002). Considering that the average pH of the North and South Saskatchewan Rivers is 8.1 and 8.3 respectively, and the dominant carbonate species is HCO₃⁻ (Stumm and Morgan, 1996), an equation similar to Helie et al. (2002) can be implemented.

From Zhang et al. (1995):

$$\epsilon_{\text{HCO}_3^- - \text{CO}_2} = -(0.141 \pm 0.003) T + (10.78 \pm 0.05) \quad (16)$$

and with an atmospheric δ¹³C of -7.0‰, the equation becomes

$$\delta_{\text{HCO}_3^-} = -(0.141 T) + 10.78 + (-7.0) \quad (17)$$

where T is the temperature in °C. Using equation (17), dissolution of atmospheric CO₂ should result in δ¹³C_{DIC} of +2.2‰ for both the North and the South Saskatchewan Rivers.

Photosynthesis and respiration are additional influential processes affecting the δ¹³C_{DIC} and CO₂ concentrations in the rivers, with the former resulting in significant fractionations of carbon isotopes. Photosynthetic and respiratory effects on δ¹³C_{DIC} are addressed more fully in a subsequent section.

The δ¹³C_{DIC} values in the North and South Saskatchewan systems show similar overall trends (Figure 21), with a decrease from approximately -7 ± 2‰ in October and November to -11 ± 1‰ in April, followed by a sudden increase to -5‰ in May and a

plateau at -4‰ throughout the summer. The $\delta^{13}\text{C}_{\text{DIC}}$ of the North Saskatchewan River is more negative, with the low values in August attributed to a large storm event that “flushed” out large quantities of groundwater from the feeder aquifers. The average $\delta^{13}\text{C}_{\text{DIC}}$ for the North and South Saskatchewan Rivers is -7.7 and -6.6‰ , respectively, indicating that the primary recharge of carbon is from soil CO_2 enriched groundwaters that reacted with limestones of the confining aquifers. The depleted $\delta^{13}\text{C}_{\text{DIC}}$ during cold season is, as for the storm event, due to larger proportional input of groundwaters into the rivers.

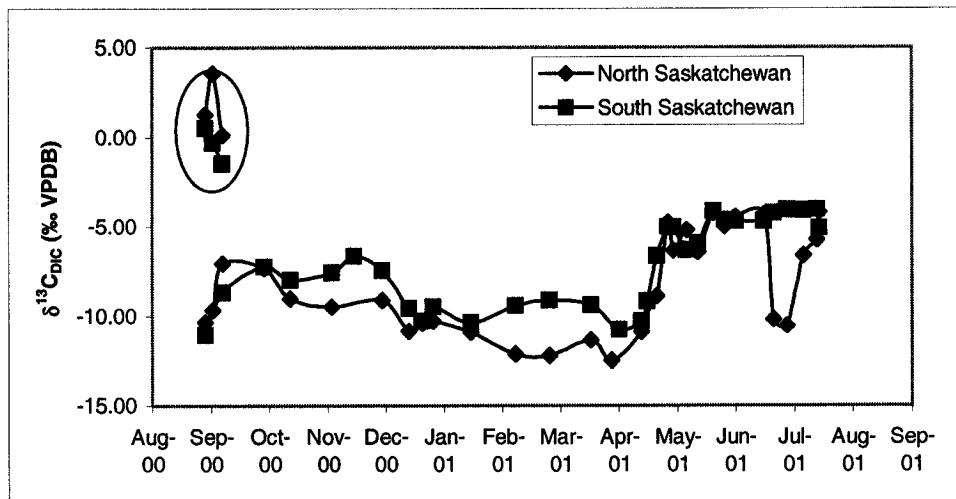


Figure 21: $\delta^{13}\text{C}_{\text{DIC}}$ in the North and South Saskatchewan Rivers. Circle indicates samples with likely field analytical error.

6.1.5 O_2 saturation and $\delta^{18}\text{O}_{\text{DO}}$

The principal mechanism controlling dissolved oxygen saturation and the isotopic composition of dissolved oxygen are atmospheric exchange (including dissolution and water turbulence) and photosynthesis/respiration. Presently, atmospheric $\delta^{18}\text{O}_{\text{DO}}$ is $+23.5\text{‰}$, a result of the Dole effect (Kroopnick and Craig, 1972; Bowen, 1988). When dissolved into water, oxygen isotopes fractionate by $+0.7\text{‰}$ (Benson and Krause, 1984), resulting in $\delta^{18}\text{O}_{\text{DO}}$ equilibrium values of $+24.2\text{‰}$.

Saturation indices of dissolved oxygen (DO) are a measure of the relative importance of photosynthesis to respiration in the system, with a saturation index of 1

usually indicative of a system in equilibrium with the atmosphere, greater than 1 reflecting supersaturation, and the dominance of respiration resulting in values of less than 1 (Quay et al., 1995).

Oxygen saturations in the North and South Saskatchewan Rivers showed similar trends throughout most of the year, except for January to March. Both rivers showed undersaturated values from September until April (Figure 22), with a short decline following the complete disappearance of ice from April to May. Subsequently, the oxygen saturation rose from ~60 up to 120% in the course of summer. The stronger oxygen depletion in winter in the North Saskatchewan River was likely due to the dominance of respiratory activities under more complete ice cover compared to the South Saskatchewan River, which remained well aerated because of the Gardiner dam and the Saskatoon weir.

$\delta^{18}\text{O}_{\text{DO}}$ will be less than +24.2‰ when ambient photosynthesis prevails over respiration because aquatic plants utilize river water for photosynthesis, with little to no fractionation (Quay et al., 1995). Thus, the photosynthetic oxygen produced will be isotopically similar to its water source oxygen, which at the latitudes of the study site are very depleted in ^{18}O due to the effect of Rayleigh distillation on precipitation (Jouzel and Merlivat, 1984).

Processes that drive $\delta^{18}\text{O}_{\text{DO}}$ towards more positive values include atmospheric exchange and community respiration. Atmospheric exchange will drive the $\delta^{18}\text{O}_{\text{DO}}$ towards +24.2‰, the equilibrium value for oxygen (Quay et al., 1995). Ecosystems dominated by respiration will have $\delta^{18}\text{O}_{\text{DO}}$ greater than +24.2‰ because the uptake of ^{16}O - ^{16}O during respiration is preferred to the uptake of ^{18}O - ^{16}O . As a result, the surrounding water becomes enriched in ^{18}O - ^{16}O (Kiddon et al., 1993), although this is not the case in an infinite reservoir.

The $\delta^{18}\text{O}_{\text{DO}}$ for the North Saskatchewan, except for the peaks in December, January, May and August, was always lower than that of the atmospheric O_2 (+24.2‰) (Figure 23). The August peak (+26.5‰) coincided with major storm events upstream. For the South Saskatchewan, the $\delta^{18}\text{O}_{\text{DO}}$ values were near atmospheric values in winter and, for the rest of the year, below the atmospheric values. The late April peak at

+25.1‰ was an exception. Particularly pronounced in both rivers was the drop in $\delta^{18}\text{O}_{\text{DO}}$ from February to March.

Plots of oxygen saturation against $\delta^{18}\text{O}_{\text{DO}}$ (Figure 24) showed a clear negative correlation with $\delta^{18}\text{O}_{\text{DO}}$ declining at increasing degree of photosynthetic production of oxygen. As discussed previously (section 4.3.1), the North and South Saskatchewan River waters have $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ of -18 to -21 ‰ and -15 to -17 ‰, respectively, which is utilized during photosynthesis to produce gaseous oxygen (Figure 11).

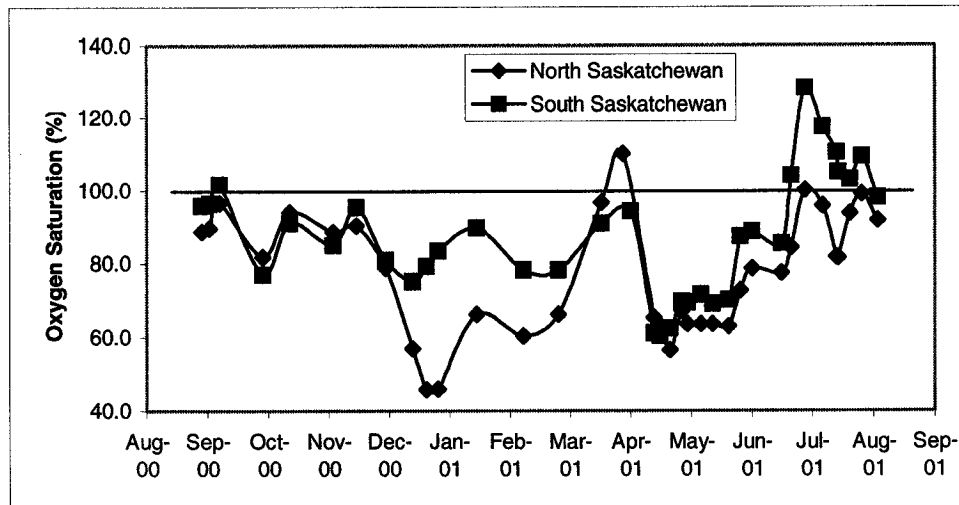


Figure 22: O_2 saturation in the North and South Saskatchewan Rivers.

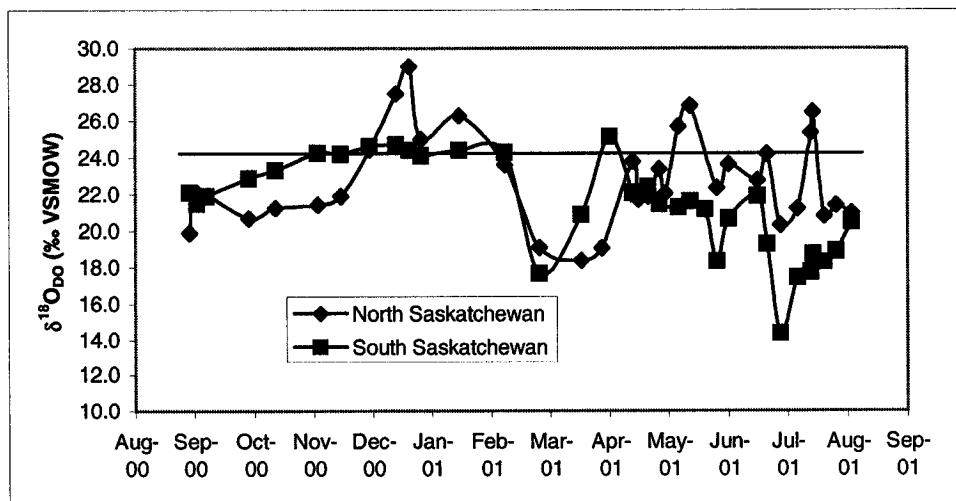


Figure 23: $\delta^{18}\text{O}_{\text{DO}}$ in the North and South Saskatchewan Rivers. Missing data has not been interpolated.

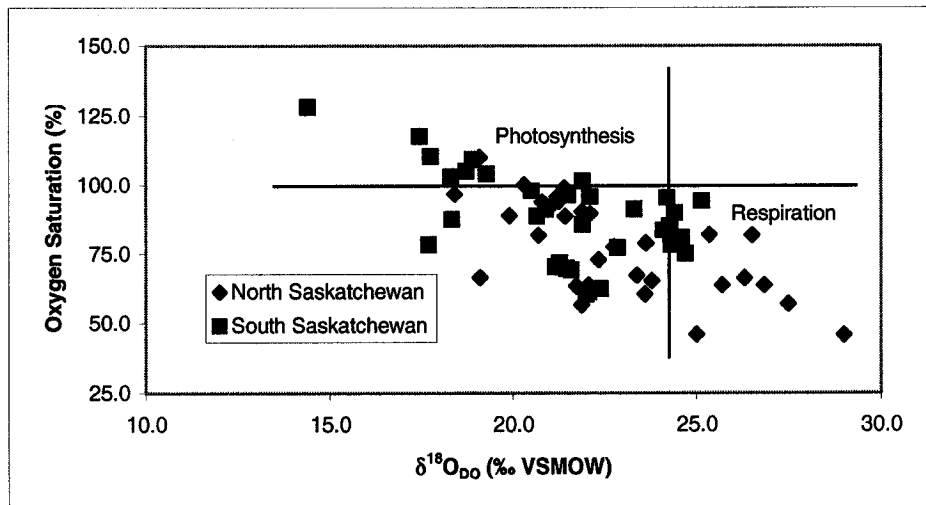


Figure 24: Scatter plot of O_{2sat} versus $\delta^{18}O_{DO}$ for the North and South Saskatchewan Rivers. Respiration and photosynthesis based on dissolved oxygen are also shown.

6.2 Factors controlling the chemistry and isotopic composition of river water

Large sets of data are often tedious and difficult to interpret. Cross-plots and graphs may provide some indication of large trends, but they are subject to focusing only on the variables being considered while the relationship to the other data is not as apparent. With the considerable number of variables measured in this study, it became inevitable that some sort of tool was needed to aid in the interpretations of the data.

Factor analysis is a statistical tool used to group large sets of data according to common characteristics or trends into 'factors'. This reduces the number of variables into a smaller set of correlated variables. Information about geological factor analysis can be found in Joreskog et al. (1976) and Davis (1986). By providing the means to divide and group large data sets according to commonalities, interpretations of the data may be simplified or enhanced. Factor analysis does not provide the explanation for the groupings, leaving the interpretations to the scientist. Therefore, an underlying knowledge of the possible causes and surrounding controls is necessary in making correct conclusions.

The factor analysis was performed using the software program SYSTAT version 10.2 (SYSTAT Inc., 2002). Ten measured variables were used and the technique utilized a multivariate approach and re-correlated the data according to the varimax rotation. This rotation groups loadings around specific factors and simplifies interpretations.

The most reliable data used is that which is directly (and confidently) measured. However, some data was acquired from large data sets and some had to be computed. Most of the data used in the following factor analyses were measured directly and, of the ten variables used, only discharge was not measured directly in this study. Discharge was acquired by using data averaged monthly over 74 years (see RivDis in Appendix 1). The discharge data was then entered according to the number of samples taken in a particular month. For example, if three samples were taken in September, the average discharge for September would be entered into a spreadsheet three times, coinciding with the dates of sampling. If only one sample was taken a month, then only one discharge value would be entered. One concern is that discharge data entered more frequently for one month than for another may weight the months differently. On the other hand, data averaged over such a long period of time can account for any irregularities that may occur during the year and should represent monthly and yearly averages. $p\text{CO}_2$ was calculated using alkalinity, pH and temperature and, therefore, was not included in the factor analysis as it is a dependent variable.

Multivariate factor analysis depends on the data set being completely randomized. The samples from the rivers were taken at the same location at similar times of the day and although the sampling periods were not definitely set, for the majority, at least one sample was taken within every two-week period. Less frequent sampling occurred in the winter when environmental conditions made sampling difficult or dangerous. On the positive side, this only added to the randomness required for factor analysis. Other than the spatial and temporal characteristics, all other variables were uncontrolled and depended on the river and the environment. When performing the analysis, the locations and times were not included while all the other variables were used. Therefore, the variables that were *not* included were those that were controlled while those that were included were uncontrolled. These measures may satisfy the randomness required.

6.2.1 The variables and factor analysis

Ten variables were analyzed in both river systems, including temperature, discharge, $\delta^{18}\text{O}_{\text{H}_2\text{O}}$, $\delta^{18}\text{O}_{\text{DO}}$, δD , $\delta^{13}\text{C}_{\text{DIC}}$, TDS, DO %, pH and alkalinity. As evident from factor analyses (Table 7, 8), some 75 to 83% of the entire variance in the measured parameters can be attributed to essentially two phenomena: seasonal variations in water budget and biological photosynthesis/respiration processes.

Variable	Seasonal	Respiration	Photosynthesis
Temperature	0.93		
Discharge	0.90		
$\delta^{18}\text{O}_{\text{H}_2\text{O}}$	0.86		
δD	0.85		
TDS	-0.80		
Alkalinity	-0.79		
$\delta^{18}\text{O}_{\text{DO}}$		0.88	
DO %		-0.84	
$\delta^{13}\text{C}_{\text{DIC}}$			0.72
pH			0.68
Total Variance	45.2	16.0	14.4

Table 7: Factor analysis for the North Saskatchewan River.

Factor 1, clearly a reflection of seasonal variations, is characterized by positive loading of temperature, discharge, $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ and $\delta\text{D}_{\text{H}_2\text{O}}$ for both rivers. TDS, on the other hand, loads on this factor positively in the South Saskatchewan River and negatively in the North Saskatchewan River. This factor does not seem to influence the alkalinity in the South Saskatchewan but in the North Saskatchewan River, the alkalinity, together with TDS, load negatively, suggesting that biological processes in the southern branch

are more pronounced. The other variables DO%, $\delta^{13}\text{C}_{\text{DIC}}$, pH, partial alkalinity and $\delta^{18}\text{O}_{\text{DO}}$ load on the remaining factors (Figure 25, 26). All these latter variables are clearly controlled by biological photosynthesis/respiration balances, both in the river itself and in the groundwater aquifers that, depending on the season, account for variable proportions of the water volume in the river. Hence the factors 1 and 2+3 are to a degree interdependent.

Despite differences in loadings on factors 1 and 2, the TDS and alkalinity were clearly interrelated (Figure 27), since HCO_3^- accounts for the bulk of TDS. The absence of correlation between discharge and alkalinity in the factor analysis for the South Saskatchewan River (Table 8) was principally due to the two September outliers. As already pointed out (section 6.2.2), these were the first measurements and analytical error cannot be entirely ruled out. Leaving aside the erroneous September data from both rivers, the negative correlation of alkalinity with discharge (Figure 28) becomes evident. At lower discharge, base flow accounts for a greater proportion of river flow, as opposed to greater contribution of overland flow to enhanced discharges during the warmer season. In general, the groundwaters that feed the base flow have higher HCO_3^- (and TDS) concentrations than their surficial counterparts.

Variable	Seasonal	Respiration	Photosynthesis
Temperature	0.93		
$\delta^{18}\text{O}_{\text{H}_2\text{O}}$	0.92		
δD	0.85		
$\delta^{18}\text{O}_{\text{DO}}$	-0.83		
TDS	0.68		
Discharge	0.61		0.62
Alkalinity		-0.93	
$\delta^{13}\text{C}_{\text{DIC}}$		0.76	
DO %		0.65	-0.58
pH			0.94
Total Variance	41.7	22.0	18.7

Table 8: Factor analysis for the South Saskatchewan River.

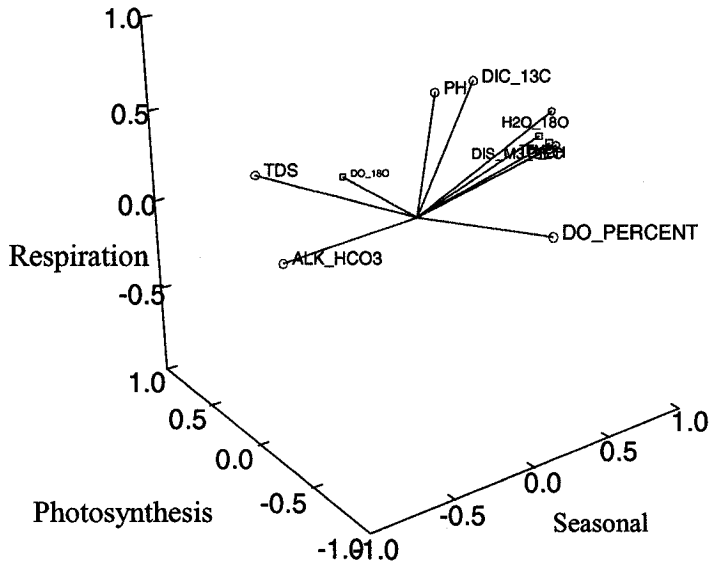


Figure 25: Triaxial plot of factor loadings for the North Saskatchewan River.

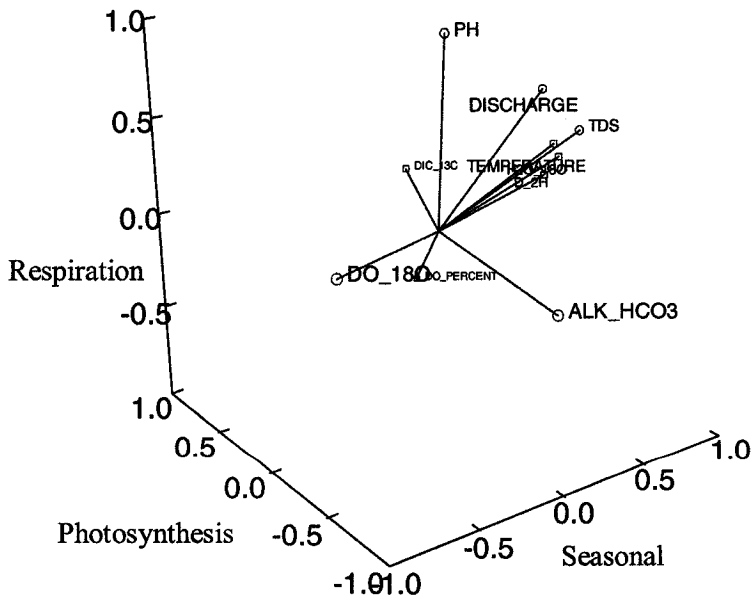


Figure 26: Triaxial plot of factor loadings for the South Saskatchewan River.

6.2.2 Factor 1: Seasonal discharge

The strong covariance of the first four variables (temperature, discharge, $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ and $\delta\text{D}_{\text{H}_2\text{O}}$) (Figure 25, 26) has a straightforward interpretation. During cold season, the discharge is reduced and most of the water originates as base flow from the feeder aquifers. Since these aquifers are recharged mostly from winter precipitation, the $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ and δD are depleted in the heavier isotopes, ^{18}O and ^2H . Rising temperatures and increasing input of overland flow result in increasing river discharge and enrichment of the water in heavier isotopes.

The negative loadings of TDS and alkalinity on the North Saskatchewan River are only a statistical artifact, perhaps due to the September outliers, clearly evident from Figures (27) and (28) that exhibit their positive covariance and a negative correlation with discharge. Rising temperatures and increased input of overland flow resulted also in greater dilution and lower alkalinity and discharge. Although the factor analysis for the South Saskatchewan River does not indicate any correlation between TDS and alkalinity when all factors are involved, there is a definite positive correlation between the two when they are separated out.

6.2.3 Factor 2 and 3: Respiration and photosynthesis processes

Factors 2 and 3 (Table 7, 8) are characterized by loadings of $\delta^{18}\text{O}_{\text{DO}}$, dissolved oxygen saturation, pH and $\delta^{13}\text{C}_{\text{DIC}}$, all variables reflecting photosynthetic and respiratory processes.

The positive loadings of $\delta^{18}\text{O}_{\text{DO}}$ and negative loadings of oxygen saturation on the same factor for the North Saskatchewan River (Table 7, Figure 25) are clearly a reflection of photosynthesis/respiration balance in the river from photosynthetic release of O_2 into the water column. The generated O_2 originates from splitting of the ambient H_2O molecules, which are depleted in ^{18}O . As a result, the greater the proportion of photosynthetic O_2 , the lighter its $\delta^{18}\text{O}_{\text{DO}}$ is (Figure 24). In contrast, respiration preferentially consumes ^{16}O - ^{16}O and drives the $\delta^{18}\text{O}_{\text{DO}}$ towards more positive values,

while simultaneously decreasing the oxygen saturation in the surrounding waters. The same processes that control the $DO/\delta^{18}O_{DO}$ in the North Saskatchewan River also control

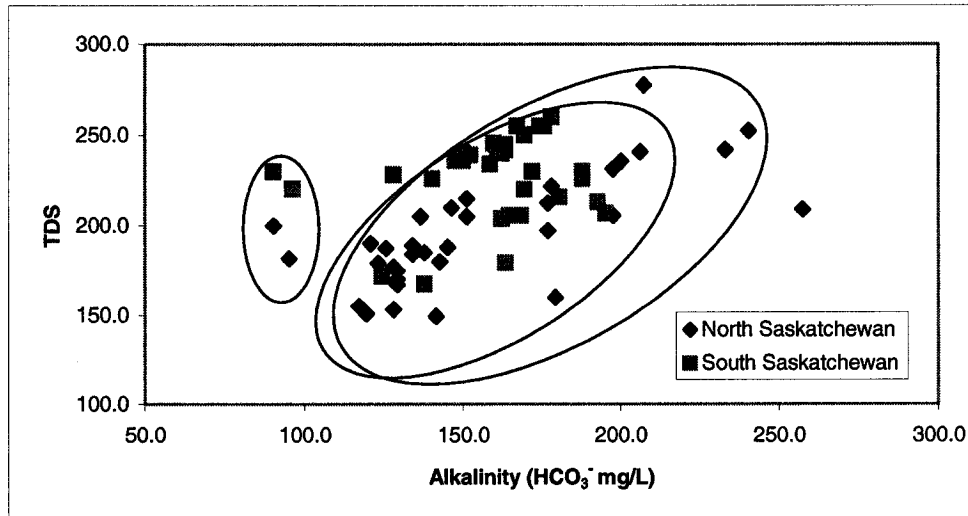


Figure 27: Alkalinity and TDS of the North and South Saskatchewan Rivers. Large circles indicate general trends while the small circle indicates outlier alkalinity points possibly due to analytical error.

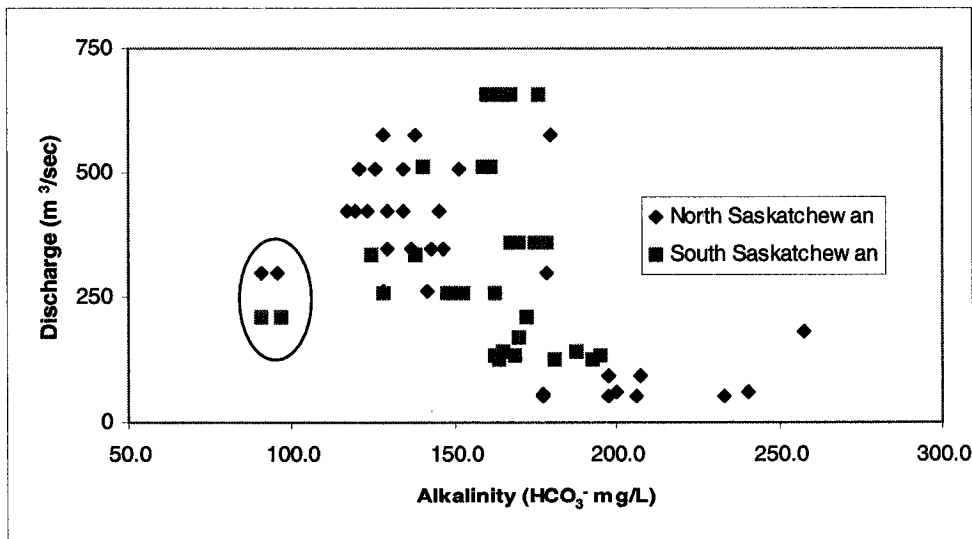


Figure 28: Discharge and alkalinity in the North and South Saskatchewan Rivers. Circle indicates September samples with possible analytical errors.

it in the South Saskatchewan River (Figure 24). The negative loading of $\delta^{18}\text{O}_{\text{DO}}$ on the factor 1 in the South Saskatchewan only signifies that the photosynthesis/respiration balance is more tightly coupled to seasonal discharge and temperature variations than is the case for the North Saskatchewan River.

The interrelationships of the remaining variables that load on factors 2 and 3 (alkalinity, pH and $\delta^{13}\text{C}_{\text{DIC}}$) are not entirely clear. The intercorrelations of these variables are mostly weighted by the September 2001 measurements, which may potentially be erroneous and their scatter plots show no discernible relationships.

6.2.4 pCO_2

Large river systems are often found to have pCO_2 concentrations well above the equilibrium with atmospheric CO_2 levels. In the Amazon, Rhine and Yangtze Rivers, pCO_2 may be ten to fifteen times higher than atmospheric values, with the Rhine and the Amazon showing mean pCO_2 's of 3300 ppm and 4000 ppm, respectively (Kempe, 1982; Gao and Kempe, 1987; Stallard, 1980). For the Amazon, Richey et al. (2002) observed that the surrounding flood plains, tributaries and the main channel were supersaturated with respect to pCO_2 , with the main channel showing values of ~ 4350 ppm. These extreme concentrations would indicate that large rivers are a source of CO_2 that evades into the atmosphere.

pCO_2 in riverine systems is an outcome of respiration activities and the degree to which they dominate the system. Values above the accepted atmospheric pCO_2 of 360 ppm are usually indicative of a net predominance of respiration and organic decay, although an increase in pCO_2 can also be attributed to greater groundwater input. In the Amazon River, pCO_2 levels are not as dependent on atmospheric exchange and groundwater inputs, but instead they are controlled mostly by ambient photosynthesis and respiration (Quay et al., 1989, 1995). In the St. Lawrence River, on the other hand, atmospheric inputs outweigh respiration and photosynthetic fluxes because of the long residence time of the bulk of its water in the Great Lakes which leads to "degassing" and exchange with the atmosphere (Yang et al., 1996; Barth and Veizer, 1999). Groundwater

input is particularly significant in winter, due to the frozen soils surrounding the river (Helie et al., 2002). Additionally, $p\text{CO}_2$ levels can decrease as water levels drop or temperature increases, thereby enhancing the degassing (Helie et al., 2002).

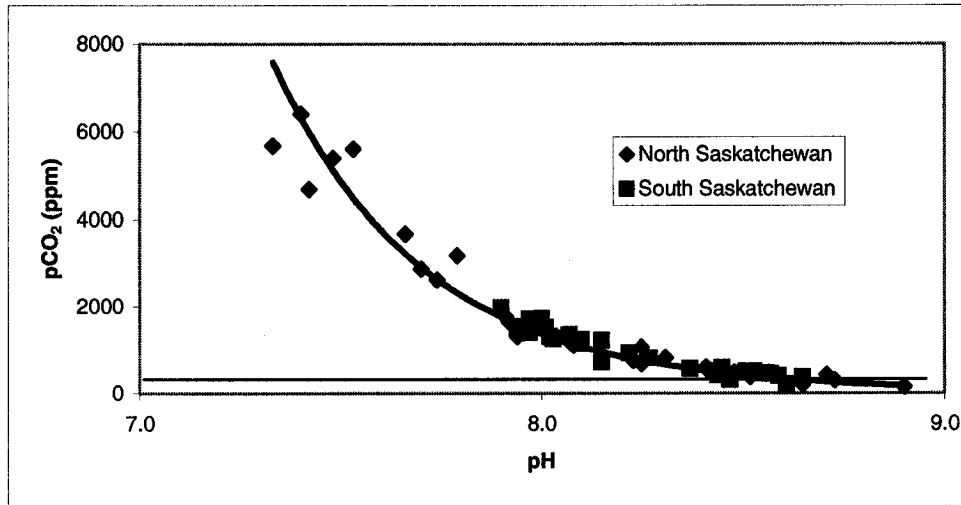


Figure 29: pH and $p\text{CO}_2$ comparisons for both river systems.

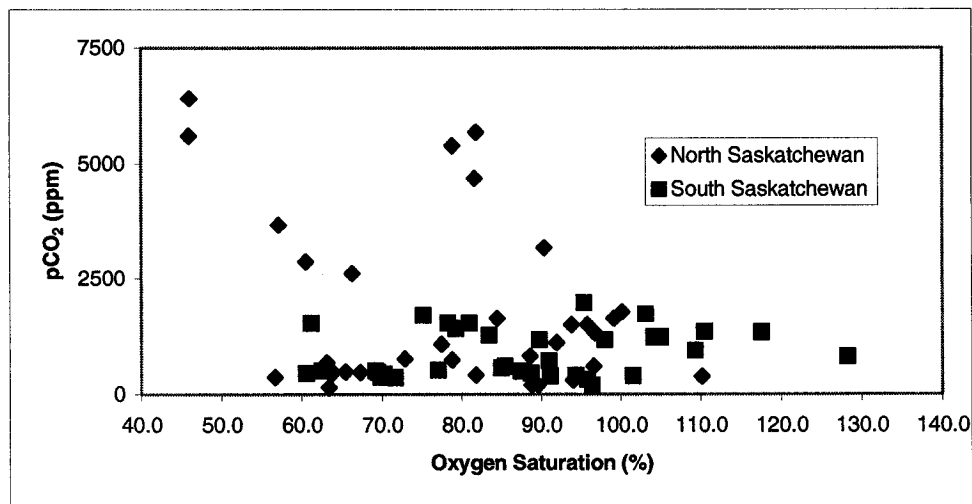


Figure 30: Comparisons between oxygen saturation and $p\text{CO}_2$ levels in both rivers.

The pH and $p\text{CO}_2$ show a near linear relationship throughout the year in the South Saskatchewan River and in the North Saskatchewan River in the summer and fall months. For the northern river, the relationship becomes concave in the winter (Figure 29). While

the pCO₂ in the North and South Saskatchewan basins show similar overall temporal trends (Figure 18), the large pCO₂ values, 10 to 18 times greater than the atmospheric levels in the winter months, were previously attributed to the ice cover that prevented degassing of CO₂ from the river into the atmosphere (Figure 29). pCO₂ increased and pH decreased during this time as the river was being supplied by base flow enriched with HCO₃⁻ charged groundwaters coupled with respiration and organic decay. This is clearly evident in Figure 30 where all highly CO₂ enriched samples are undersaturated with respect to dissolved oxygen.

6.3 Respiration/Photosynthesis (R:P)

Quay et al. (1989, 1995) (equation 18-21) utilized $\delta^{18}\text{O}_{\text{DO}}$, $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ and oxygen saturation to estimate the relative importance of respiratory and photosynthetic activities within a river. The systems with an R:P <1 are dominated by photosynthesis and those with >1 by respiration. The generalized R:P graph is depicted in Figure 31 with the approach based on a grid of $\delta^{13}\text{C}_{\text{DIC}}$ and $\delta^{18}\text{O}_{\text{DO}}$ values, the photosynthesis driving the data towards the upper left corner and respiration in the opposite direction. Exchange with atmospheric oxygen, on the other hand, is independent of the carbon variable and therefore shifts the data upwards. Despite large dispersion, the scatter diagram of $\delta^{13}\text{C}_{\text{DIC}}/\delta^{18}\text{O}_{\text{DO}}$ values in the Saskatchewan Rivers shows a somewhat comparable pattern (Figure 32) to the one expected from the theoretical consideration.

Rivers often show high R:P ratios (Wang and Veizer, 2000) because the sediments suspended in the water column never get the chance to settle out. The increased sediment load offers increased surface area to microbes that can attach themselves and remain in the water column, thus enhancing the respiration in the basin (Wissmar et al., 1981). In addition, the increased sediment load retards photosynthesis (Vannote et al., 1980) by limiting the depth of light penetration. Small rivers and streams are often dominated by organic material entering from terrestrial sources (such as leaves and twigs) while phytoplankton and plants play an enhanced role in large rivers. This enhanced impact of biota allows respiration to exceed photosynthesis in large river systems (Schlesinger, 1997).

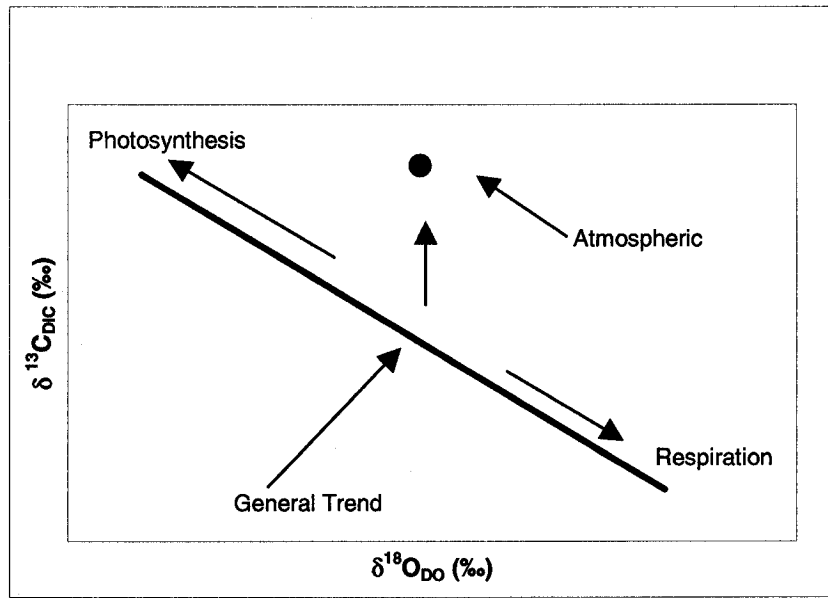


Figure 31: Generalized respiration/photosynthesis relationship.

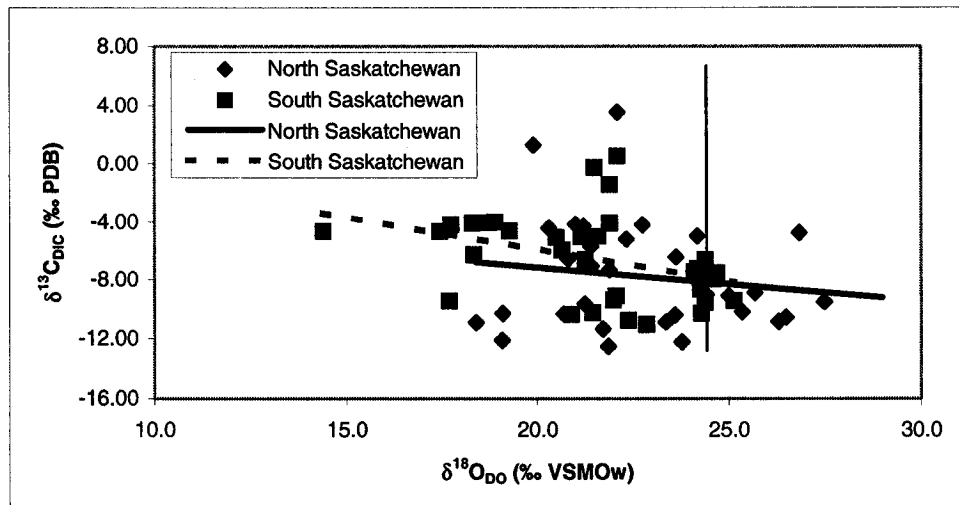


Figure 32: Respiration/photosynthesis trends in the North and South Saskatchewan Rivers.

Respiration, photosynthesis and atmospheric gas exchanges are the three primary mechanisms controlling the amount of carbon dioxide present in an aquatic system. Assuming no gas exchange with the atmosphere (as ascertained by $\delta^{13}\text{C}_{\text{DIC}}$ values), the application of oxygen isotopes ($\delta^{18}\text{O}_{\text{H}_2\text{O}}$, $\delta^{18}\text{O}_{\text{DO}}$) and of dissolved oxygen concentrations

(O_{2sat}), enables quantification of respiration/photosynthesis ratios (R:P). The system thus can be classified as predominantly respiratory or photosynthetic, although seasonal fluctuations may exist.

Respiration and photosynthesis can be calculated as (Quay et al., 1995):

$$d(O_2)/dt = G/Z * (O_{2sat} - O_2) - R + P \quad (18)$$

and

$$d(^{18}O_2)/dt = G/Z * \alpha_s * (^{18}O/^{16}O) - O_2 * (^{18}O/^{16}O) - R * \alpha_r * (^{18}O/^{16}O) + P * \alpha_p * (^{18}O/^{16}O)_w \quad (19)$$

where G is the gas transfer rate, Z is the depth, O_{2sat} is DO saturation, O_2 is the DO concentration in mg/L, R is the respiration rate, P is the photosynthetic rate, α_g is the gas transfer ratio of $^{18}O^{16}O$ to $^{16}O_2$ and equals 0.9972 (Knox et al., 1992), α_s is the solubility ratio of $^{18}O^{16}O$ to $^{16}O_2$ gases in the water and is equal to 1.0008 at 20°C (Benson and Krause, 1984; Jahne et al., 1987), α_r is the ratio of respiratory $^{18}O^{16}O$ to $^{16}O_2$ and is equal to 0.982 (Quay et al., 1995), α_p is the ratio of photosynthetic $^{18}O^{16}O$ to $^{16}O_2$, $^{18}O/^{16}O$ is the isotopic ratio of dissolved oxygen, a is atmosphere and w is water. At steady state, equations (18) and (19) can be reduced to

$$R/P = (\alpha_p * (^{18}O/^{16}O)_w - (^{18}O/^{16}O)_g) / \alpha_r * (^{18}O/^{16}O) - (^{18}O/^{16}O)_g \quad (20)$$

Where

$$(^{18}O/^{16}O)_g = [\alpha_g * (\alpha_s * (^{18}O/^{16}O)_a - (O_2/O_{2sat}) * (^{18}O/^{16}O))] / [1 - (O_2/O_{2sat})] \quad (21)$$

The calculated ratio of respiration to photosynthesis depends primarily on the isotopic compositions of oxygen and its saturation level (equation 20) (Quay et al., 1995). A ratio greater than one indicates respiratory dominance, less than one indicates photosynthetic dominance.

Using equations (20) and (21) to calculate R:P for September 18/01 for the North Saskatchewan basin results in:

$$R/P=(1*0.001968702-0.002118268)/0.982*0.002045103-0.002118268)=1.36$$

The same date for the South Saskatchewan shows that:

$$R/P=(1*(0.001972743-0.0021494121)/0.982*0.00209515-0.0022149412)=1.29$$

The North and South Saskatchewan Rivers both have average respiration/photosynthesis ratios of 2.3 and 1.6, respectively, indicating that both systems are respiration dominated throughout the year, with higher ratios found in the winter and lower ratios in the summer months (Figure 33). In the North Saskatchewan River, the apparent photosynthetic signature in April was accounted for by enhanced oxygen invasion into the colder river water when it was exposed to the atmosphere when the ice melted. Storm events accounted for the large respiration signal in the North Saskatchewan River. Respiration/photosynthesis ratios decrease with decreasing pCO₂ and increase with decreasing oxygen saturation (Figures 34, 35), both the result of respiration in the system.

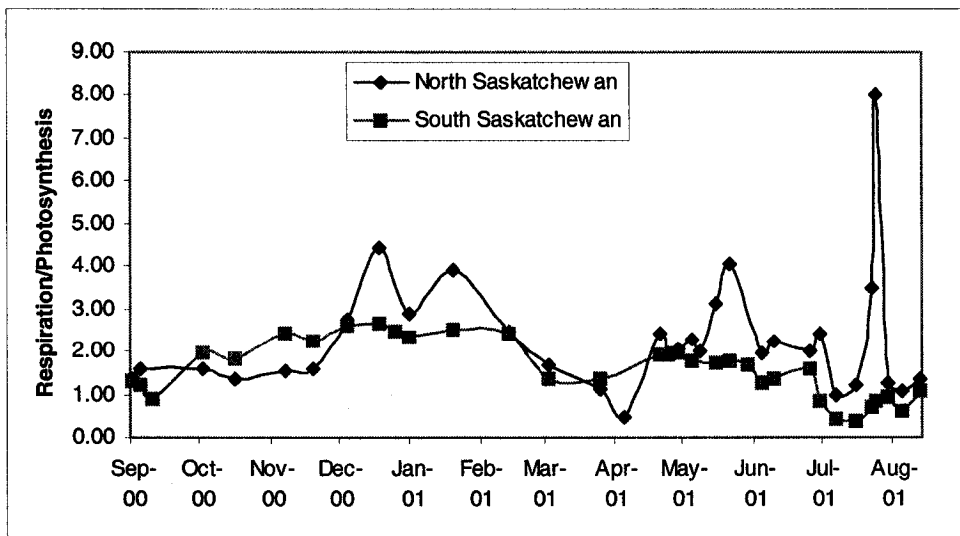


Figure 33: Respiration/photosynthesis ratios of the North and South Saskatchewan Rivers.

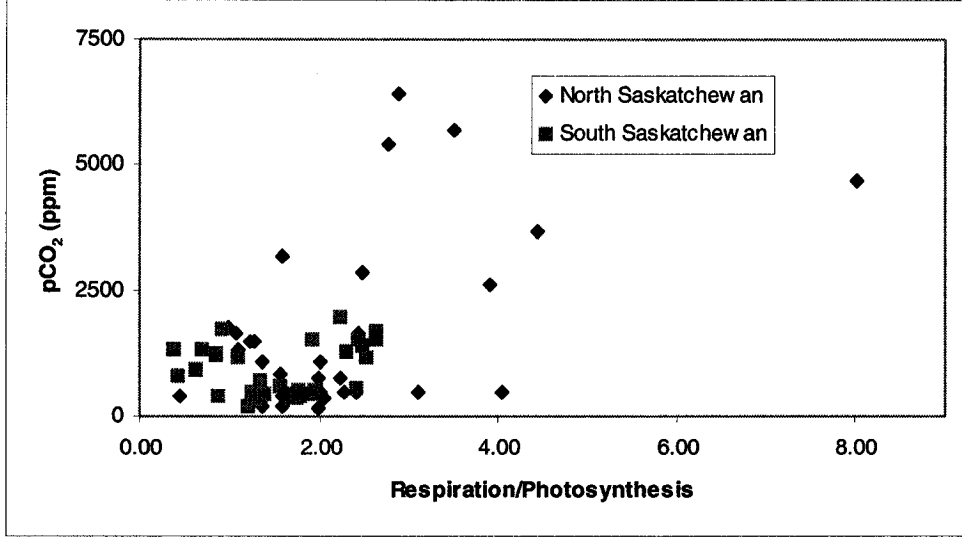


Figure 34: The relationship between pCO₂ and respiration/photosynthesis in both river systems.

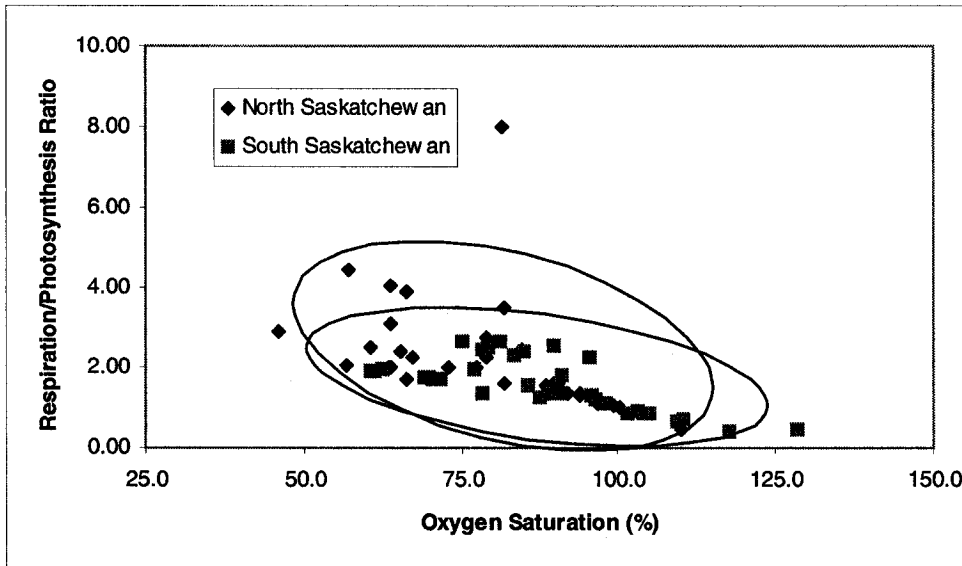


Figure 35: Oxygen saturation in relation to respiration/photosynthesis in the North and South Saskatchewan Rivers.

6.3.1 Uncertainties

The above calculations of respiration/photosynthesis ratios are beset by several uncertainties. Small errors may be associated with the calculation of $p\text{CO}_2$, particularly for values from May 22, 2001 until August 9, 2001 where a correction factor was applied due to a faulty membrane in the oxygen probe. Measurements prior to May and those from July 12 were taken with the Hydrolab and are considered correct, and an additional measurement was taken on August 10 for comparison with the measurement taken on August 9. These measurements were used to develop a correction factor that was applied to the oxygen saturation values.

In Quay's equation (20), the right hand side of the equation carries most of the uncertainty. The main problem lies in the denominator of equation (21). If dissolved oxygen concentration approaches saturation, the denominator will become 1 and this results in an undefined equation. Such would be particularly the case in systems where oxygen is found in low concentrations at high saturations. Another error arises from the fact that the α variables are often those at 20°C. This error is, however, relatively small. Additionally, the dissolved oxygen concentrations on the left hand side of the equation are assumed to be at steady state. In order for this assumption to be valid, I had to assume that the rate of change in oxygen concentrations was ~1% of the oxygen flux due to discharge or respiration, with the result that the respiration/photosynthesis ratio becomes independent of the air-water exchange rate through equation (21). During ice cover, the steady state assumption is modified by discounting the atmospheric exchange. However, river systems are complex and the models for moving water will always have to account for complex and ill-defined variables.

In Zhang's equation (17), the main possibility for error lies in the value chosen to represent the atmospheric $\delta^{13}\text{C}$ that may vary between -6‰ and -8‰. Intermediate results were received using -7‰.

6.3.2 Summary of respiration/photosynthesis ratios

Factor analyses indicates that water characteristics for both the North and South Saskatchewan River basins are controlled by two major phenomena: seasonal variations and respiratory/photosynthetic activities. The primary seasonal difference between the two watersheds is their relative dependence on base flow to maintain the river volumes, with the South Saskatchewan River showing more reliance than the North. $p\text{CO}_2$ measurements confirm base flow dependence as higher concentrations of $p\text{CO}_2$ and TDS are present in the colder months when there is little precipitation or recharge other than groundwater.

Additionally, both watersheds are respiration dominated throughout the year. Increases in photosynthesis in the summer months are accompanied by increases in respiration.

Chapter 7

CONCLUSIONS

The purpose of this thesis was to obtain a first order estimate as to what extent Prairie dominated ecosystems, such as the North and South Saskatchewan River basins, could be a source or sink of atmospheric carbon dioxide. Carbon and water fluxes are coupled through respiration and photosynthesis, the latter at a specific H₂O/CO₂ ratio called "water utilization efficiency". Knowing the hydrological budget of a watershed, it is possible to calculate its net primary productivity (NPP). This estimate, combined with heterotrophic soil respiration (R_h) taken from biological model data, enables evaluation of the capability of a given watershed to serve as a net sink or source of atmospheric CO₂. The parameter of the hydrological budget that is essential for calculation of NPP is the transpiration flux. This can be estimated by subtracting the annual discharge, evaporation and interception from the yearly precipitation input.

In the North Saskatchewan watershed, 52.63 km³ of water is input into the basin through precipitation. Of this, ~15% (7.73 km³) was directly discharged out of the basin, ~11% (5.85 km³) was evaporated, ~16% (8.63 km³) was intercepted and ~58% (30.4 km³) was transpired. In the South Saskatchewan watershed, of the 61.98 km³ input through precipitation, ~14% (8.83 km³) was directly discharged, ~12% (7.56 km³) was evaporated, ~16% (9.77 km³) was intercepted and ~58% (35.8 km³) was transpired. It is apparent that the largest loss of water from both basins is through transpiration.

Using the above transpiration fluxes and water use efficiency values of 990 for the North Saskatchewan River and 998 for the South Saskatchewan River, the calculated NPP are 0.0203 and 0.0241 Pg C/a for the North and South Saskatchewan Rivers, respectively. These are comparable to the respective literature heterotrophic respiration fluxes (R_h) of 0.0204 and 0.0266 Pg C/a, suggesting that photosynthesis and respiration are in balance and the two watersheds are not sources or sinks of atmospheric CO₂.

For the aquatic systems of the North and South Saskatchewan Rivers, statistical analysis of water chemistry (discharge, pH, alkalinity, temperature, TDS, δ¹⁸O_{H₂O}, δD,

$\delta^{18}\text{O}_{\text{DO}}$, $\delta^{13}\text{C}_{\text{DIC}}$ and DO %) showed that seasonal variations and photosynthesis/respiration processes accounted for approximately 40 and 30% of the entire variance, respectively. However, seasonality, photosynthesis and respiration appeared to be more closely related in the South Saskatchewan than in the North Saskatchewan River. Seasonal variations (increasing overland input to base flow during warmer seasons) resulted in higher discharge, less negative $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ and δD (base flow is due primarily to winter recharge) as well as lower TDS and alkalinity (from dilution by overland flow). Photosynthetic and respiratory processes in the river controlled the dissolved oxygen saturation, $\delta^{18}\text{O}_{\text{DO}}$ and $\delta^{13}\text{C}_{\text{DIC}}$. The pCO_2 levels during the winter months were 10 to 18x above the atmospheric equilibrium values, particularly in the North Saskatchewan River where the ice cover in winter was complete. In the South Saskatchewan River, the Gardiner dam and the Saskatoon weir prevented total freezing, thus enabling CO_2 evasion into the atmosphere. Throughout the year, the R:P ratio was greater than 1 in both rivers. In order to sustain this respiratory dominance, the aquatic system must be supplied by an external source of carbon, likely from ground water recharge, as indicated by an average $\delta^{13}\text{C}_{\text{DIC}}$ of $\sim -7\text{‰}$.

The terrestrial portion of a watershed is clearly the dominant factor in determining whether it is a source or sink for atmospheric CO_2 . Although the aquatic portions of the watersheds are dominated by respiration throughout the year, they only account for a small part of the larger watershed and their impact on the carbon cycle is orders of magnitudes less than that exhibited by the terrestrial portion.

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Appendices

Appendix 1: Databases

Base Maps

The "Gross Watershed Boundaries for the Prairies" project was produced in conjunction with the Water Survey of Environment Canada and the Prairie Farm Rehabilitation Administration (PFRA). Later, the project's jurisdiction was given to the PFRA. The project consists of a digital compilation of drainage basin boundaries and gauging stations, including NTS maps and multiple overlays. Primarily, this data set provided the base maps used in Arc View and can be found online at <http://www.agr.gc.ca/pfra/gis/gwshed.htm>.

Precipitation

Precipitation in the North and South Saskatchewan basins was calculated using the "Legates surface and ship observation of precipitation" database produced by Legates and Wilmott (1990), covering up to 60 years (1920 to 1980) worth of worldwide precipitation. The database is based on a 0.5° x 0.5° worldwide grid and was clipped in Arc View using the North and South Saskatchewan basin boundary files created using the PFRA's Gross Watershed Boundaries project. The database was converted from mm/month to km³/a to facilitate ease of comparison with other hydrometric volumes in the basin. The database can be found online at <ftp://daac.gsfc.nasa.gov/data/hydrology/precip/legates>.

Soil CO₂ Data

The soil CO₂ emissions database was compiled by Raich and Potter (1995) and covers a 0.5 x 0.5° latitudinal/longitudinal grid. It is comprised both of root respiration and soil organism respiration. Both temperature and precipitation were correlated with the soil emissions. The database can be found online at <ftp://cdiac.esd.ornl.gov/pub/db1015>.

Discharge Data

Discharge at the mouths of the North and South Saskatchewan Rivers was determined using the HYDAT CD-ROM data archive and RIVDIS data files compiled by Vörösmarty et al. (1998) found online at <http://www-eosdis.ornl.gov/daacpages/rivdis.html>. HYDAT data, covering a minimum of 30 years, was converted from monthly measurements into km³/a and had good agreement with the RIVDIS data set.

Temperature Data

The "Terrestrial air temperature and precipitation: Monthly and annual time series (1950-1999)" database was produced by Wilmott and Matsuura (2001) and covers almost fifty years worth of data. Data was available in monthly and yearly averages and, therefore, needed no conversion. The temperature data is mandatory for calculating the equilibrium fractionation factors used to determine the percentage of input that is lost as evaporation. Also, it is useful in interpreting the effect of local climatic conditions found in the basin. The database can be accessed online at http://climate.geog.udel.edu/~climate/html_pages/download.html#ghcn_T_P_clim.

Humidity Data

Humidity data was also needed to determine the percent evaporation found in the basins. Unfortunately, humidity data for Canada is scarcer and is not commonly based on grid type coverage. As a result, the complete average of the unevenly spaced data was taken for each basin and applied as a whole. Luckily, the range of the humidity data was small. The data was taken from the Canadian Monthly Climate Data (1961-1990) Normals found on CD-ROM and adjusted to represent an annual percentage value. Additionally, this data can be found online at <http://sis.agr.gc.ca/cansis/nsdb/ecostrat/district/climate/html>.

Land Cover Database

The North America Land Cover Database Version 2.0 is produced by the USGS and divided into several overlays, including the North America Seasonal Land Cover Regions file, the Simple Biosphere 2 Model and the Running Vegetation Life forms files. The legends for these files were downloaded and cross-referenced in order to reclassify the files. The land cover files can be downloaded at http://edcdaac.usgs.gov/glcc/na_int.html. FLUXNET can be downloaded at <http://public.ornl.gov/fluxnet/dataindex.cfm>.

Global Primary Production Data Initiative

The GPPDI is a 0.5 x 0.5 grid comparing net primary productivity, temperature and precipitation and resulting in a multi-biome classification scheme. The files were produced at the Oak Ridge National Laboratory Distributed Active Archive Center and can found online at <http://www.daac.ornl.gov/>

Appendix 2: $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ and δD of Water Samples (in ‰ VSMOW)

North Saskatchewan

Date	$\delta^{18}\text{O}_{\text{H}_2\text{O}}$	δD	Temperature (C)
18-Sep-00	-18.2	-145	15.1
22-Sep-00	-18.0	-143	9.6
27-Sep-00	-17.9	-144	9.5
19-Oct-00	-18.4	-145	5.8
2-Nov-00	-19.0	-152	3.0
24-Nov-00	-19.7	-155	-0.2
6-Dec-00	-20.2	-159	-0.3
21-Dec-00	-20.6	-154	-0.3
4-Jan-01	-19.4	-149	-0.3
11-Jan-01			-0.3
17-Jan-01	-20.5	-157	-0.3
6-Feb-01	-20.5	-158	-0.3
2-Mar-01	-20.6	-160	-0.3
20-Mar-01	-20.3	-158	-0.2
11-Apr-01	-19.5	-153	-0.2
22-Apr-01	-19.2	-151	8.9
8-May-01	-18.7	-149	13.2
11-May-01	-18.7	-151	13.7
16-May-01	-18.6	-148	14.6
22-May-01	-18.5	-149	13.4
25-May-01	-18.3	-148	17.5
1-Jun-01	-17.7	-146	13.6
7-Jun-01	-18.1	-147	16.6
15-Jun-01	-18.3	-147	18.8
21-Jun-01	-18.4	-149	20.0
27-Jun-01	-18.2	-149	17.6
12-Jul-01	-18.4	-146	23.0
17-Jul-01	-17.6	-142	22.5
24-Jul-01	-17.7	-144	21.1
2-Aug-01	-18.0	-143	22.2
9-Aug-01	-18.0	-142	20.6
10-Aug-01	-18.1	-139	20.3
16-Aug-01	-17.8	-140	21.6
22-Aug-01	-17.6	-140	21.6
30-Aug-01	-18.0	-144	17.9

South Saskatchewan

Date	$\delta^{18}\text{O}_{\text{H}_2\text{O}}$	δD	Temperature (C)
18-Sep-00	-16.2	-131	15.5
22-Sep-00	-16.3	-132	9.5
27-Sep-00	-16.3	-131	10.4
19-Oct-00	-16.7	-135	7.2
2-Nov-00	-16.5	-133	3.4
24-Nov-00	-16.7	-135	-0.2
6-Dec-00	-16.8	-134	-0.3
21-Dec-00	-16.8	-130	-0.3
4-Jan-01	-16.8	-133	-0.3
11-Jan-01	-16.6	-133	-0.3
17-Jan-01	-16.5	-132	-0.3
6-Feb-01	-16.7	-135	-0.3
2-Mar-01	-16.7	-136	-0.3
20-Mar-01	-16.5	-133	-0.3
11-Apr-01	-16.2	-134	-0.3
26-Apr-01	-15.6	-128	-0.1
8-May-01	-15.7	-129	13.1
11-May-01	-15.8	-130	15.2
16-May-01	-15.5	-129	14.5
22-May-01	-15.7	-131	13.3
25-May-01	-15.8	-131	18.4
1-Jun-01	-15.7	-130	14.8
7-Jun-01	-15.5	-129	17.6
15-Jun-01	-15.4	-127	19.2
21-Jun-01	-15.8	-130	21.1
27-Jun-01	-15.7	-130	17.2
12-Jul-01	-14.9	-125	22.3
17-Jul-01	-15.0	-126	23.1
24-Jul-01	-15.0	-128	23.3
2-Aug-01	-15.3	-126	24.0
9-Aug-01	-15.3	-127	20.6
10-Aug-01	-15.2	-125	20.4
16-Aug-01	-15.2	-128	22.3
22-Aug-01	-15.3	-128	22.3
30-Aug-01	-15.3	-130	17.3

Appendix 3: List of isotope and chemical data utilized in calculation of R:P ratios

North Saskatchewan

Date	$\delta^{18}\text{O}_{\text{H}_2\text{O}}$ (VSMOW)	$\delta^{13}\text{C}_{\text{DIC}}$ (VPDB)	$\delta^{18}\text{O}_{\text{DO}}$ (VSMOW)	DO%	pCO ₂ (ppm)	R:P Ratio
18-Sep-00	-18.2	1.3	19.9	88.8	312	2.32
22-Sep-00	-18.0	3.6	22.1	89.6	194	2.42
27-Sep-00	-17.9	0.2		96.6	391	
19-Oct-00	-18.4	-10.3	20.7	81.8	524	2.37
2-Nov-00	-19.0	-9.6	21.3	94.0	398	2.44
24-Nov-00	-19.7	-7.1	21.4	88.6	572	2.49
6-Dec-00	-20.2	-7.3	21.9	90.4	1976	2.55
21-Dec-00	-20.6	-9.0	24.4	78.9	1528	2.71
4-Jan-01	-19.4	-9.5	27.5	57.1	1703	2.77
11-Jan-01			29.0	45.9	1416	
17-Jan-01	-20.5	-9.1	25.0	46.0	1279	2.73
6-Feb-01	-20.5	-10.8	26.3	66.3	1168	2.79
2-Mar-01	-20.6	-10.4	23.6	60.5	1530	2.67
20-Mar-01	-20.3	-10.3	19.1	66.4		2.41
11-Apr-01	-19.5	-10.9	18.4	96.7	717	2.31
22-Apr-01	-19.2	-12.1	19.1	110.1	408	2.33
8-May-01	-18.7	-12.2	23.8	65.4	782	2.56
11-May-01	-18.7	-11.3	21.7	63.4	457	2.47
16-May-01	-18.6	-12.5	21.9	56.6	511	2.47
22-May-01	-18.5	-10.9	23.4	67.3	368	2.52
25-May-01	-18.3	-9.3	22.1	63.7	472	2.46
1-Jun-01	-17.7	-8.9	25.7	63.8	354	2.57
7-Jun-01	-18.1	-4.8	26.8	63.8	513	2.64
15-Jun-01	-18.3	-6.3		63.1	446	3.10
21-Jun-01	-18.4	-5.2	22.3	72.9	504	2.47
27-Jun-01	-18.2	-6.4	23.6	78.8	453	2.51
12-Jul-01	-18.4	-4.2	22.8	77.5	597	2.49
17-Jul-01	-17.6	-5.0	24.2	84.5	1224	2.50
24-Jul-01	-17.7	-4.4	20.3	100.1	811	2.31
2-Aug-01	-18.0	-4.3	21.2	95.8	1328	2.38
9-Aug-01	-18.0	-10.2	25.4	81.9	1345	2.58
10-Aug-01	-18.1	-10.5	26.5	81.7	1231	2.64
16-Aug-01	-17.8	-6.6	20.8	93.8	1723	2.34
22-Aug-01	-17.6	-5.7	21.4	99.1	944	2.36
30-Aug-01	-18.0	-4.1	21.0	91.9	1173	2.37

South Saskatchewan

Date	$\delta^{18}\text{O}_{\text{H}_2\text{O}}$ (VSMOW)	$\delta^{13}\text{C}_{\text{DIC}}$ (VPDB)	$\delta^{18}\text{O}_{\text{DO}}$ (VSMOW)	DO%	pCO ₂ (ppm)	R:P Ratio
18-Sep-00	-16.2	0.5	22.1	95.8	202	2.30
22-Sep-00	-16.3	-0.3	21.5	96.4	194	2.27
27-Sep-00	-16.3	-1.5	21.9	101.5	606	2.29
19-Oct-00	-16.7	-11.1	22.9	77.1	421	2.37
2-Nov-00	-16.5		23.3	91.1	302	2.38
24-Nov-00	-16.7	-8.6	24.3	85.0	827	2.45

6-Dec-00	-16.8	-7.2	24.2	95.4	3173	2.45
21-Dec-00	-16.8	-8.0	24.6	81.0	5394	2.47
4-Jan-01	-16.8	-7.5	24.7	75.2	3672	2.48
11-Jan-01	-16.6	-6.6	24.4	79.3	5599	2.45
17-Jan-01	-16.5	-7.4	24.1	83.5	6406	2.42
6-Feb-01	-16.7	-9.5	24.4	89.8	2621	2.46
2-Mar-01	-16.7	-10.3	24.3	78.3	2874	2.45
20-Mar-01	-16.5	-9.5	17.7	78.3		2.07
11-Apr-01	-16.2	-10.3	20.9	91.0	1323	2.23
26-Apr-01	-15.6	-9.4	25.1	94.3	386	2.43
8-May-01	-15.7	-9.1	22.1	61.2	489	2.28
11-May-01	-15.8	-9.4	22.0	60.5	151	2.29
16-May-01	-15.5	-10.8	22.4	62.5	368	2.29
22-May-01	-15.7	-10.3	21.5	69.8	480	2.25
25-May-01	-15.8	-9.2		69.5	501	
1-Jun-01	-15.7	-6.6	21.3	71.7	465	2.23
7-Jun-01	-15.5	-5.0	21.6	69.2	487	2.24
15-Jun-01	-15.4	-5.0	21.2	70.3	684	2.22
21-Jun-01	-15.8	-6.3	18.3	87.4	760	2.08
27-Jun-01	-15.7	-5.9	20.7	88.7	746	2.19
12-Jul-01	-14.9	-4.1	21.9	85.5	1080	2.22
17-Jul-01	-15.0	-4.6	19.3	104.1	1640	2.07
24-Jul-01	-15.0	-4.7	14.4	128.3	1770	1.77
2-Aug-01	-15.3	-4.7	17.5	117.5	1500	1.98
9-Aug-01	-15.3	-4.2	17.8	110.4	5675	2.00
10-Aug-01	-15.2	-4.0	18.7	105.0	4688	2.05
16-Aug-01	-15.2	-4.1	18.3	103.1	1491	2.03
22-Aug-01	-15.3	-4.0	18.9	109.3	1635	2.07
30-Aug-01	-15.3	-5.1	20.5	98.0	1109	2.15

Appendix 4: River Chemistry

North Saskatchewan

Date	pH	Alkalinity (HCO ₃ ⁻)	Discharge (m ³ /s)	Temperature (C)	TDS
18-Sep-00	8.7	95	296.6	15.1	182
22-Sep-00	8.6	90	296.6	9.6	200
27-Sep-00	8.4	178	296.6	9.5	222
19-Oct-00	8.7	257	183.0	5.8	209
2-Nov-00	8.7	198	91.8	3.0	206
24-Nov-00	8.3	207	91.8	-0.2	278
6-Dec-00	7.8	240	61.4	-0.3	253
21-Dec-00	7.5	200	61.4	-0.3	236
4-Jan-01	7.7	206	52.6	-0.3	241
11-Jan-01	7.5	233	52.6	-0.3	242
17-Jan-01	7.4	198	52.6	-0.3	231
6-Feb-01	7.7	177	53.6	-0.3	197
2-Mar-01	7.7	177	56.9	-0.3	213
20-Mar-01	7.6		56.9	-0.2	210
11-Apr-01	7.9	142	261.2	-0.2	149
22-Apr-01	8.5	128	261.2	8.9	153
8-May-01	8.4	143	348.5	13.2	180
11-May-01	8.9	129	348.5	13.7	170
16-May-01	8.5	129	348.5	14.6	175
22-May-01	8.4	137	348.5	13.4	205
25-May-01	8.5	146	348.5	17.5	210
1-Jun-01	8.5	151	507.8	13.6	215
7-Jun-01	8.5	151	507.8	16.6	205
15-Jun-01	8.3	121	507.8	18.8	190
21-Jun-01	8.2	126	507.8	20.0	188
27-Jun-01	8.3	134	507.8	17.6	189
12-Jul-01	8.3	179	578.1	23.0	160
17-Jul-01	7.9	128	578.1	22.5	177
24-Jul-01	7.9	138	578.1	21.1	185
2-Aug-01	7.9	123	421.8	22.2	179
9-Aug-01	7.3	117	421.8	20.6	155
10-Aug-01	7.4	120	421.8	20.3	151
16-Aug-01	8.0	129	421.8	21.6	167
22-Aug-01	8.0	145	421.8	21.6	188
30-Aug-01	8.1	134	421.8	17.9	184

South Saskatchewan

Date	pH	Alkalinity (HCO ₃ ⁻)	Discharge (m ³ /s)	Temperature (C)	TDS
18-Sep-00	8.5	96	207.7	15.5	221
22-Sep-00	8.6	90	207.7	9.5	230
27-Sep-00	8.6	172	207.7	10.4	230
19-Oct-00	8.4	170	168.7	7.2	220
2-Nov-00	8.6	188	140.1	3.4	226

24-Nov-00	8.4	165	140.1	-0.2	206
6-Dec-00	7.9	193	126.0	-0.3	213
21-Dec-00	7.9	163	126.0	-0.3	179
4-Jan-01	8.0	195	131.2	-0.3	207
11-Jan-01	8.0	162	131.2	-0.3	204
17-Jan-01	8.0	168	131.2	-0.3	206
6-Feb-01	8.1	181	125.2	-0.3	216
2-Mar-01	8.0	188	140.9	-0.3	230
20-Mar-01	8.2		140.9	-0.3	155
11-Apr-01	8.2	124	336.5	-0.3	172
26-Apr-01	8.4	138	336.5	-0.1	168
8-May-01	8.0	170	359.3	13.1	250
11-May-01	8.6	174	359.3	15.2	255
16-May-01	8.5	176	359.3	14.5	255
22-May-01	8.7	178	359.3	13.3	260
25-May-01	8.6	167	359.3	18.4	255
1-Jun-01	8.7	167	657.8	14.8	255
7-Jun-01	8.5	176	657.8	17.6	255
15-Jun-01	8.6	163	657.8	19.2	245
21-Jun-01	8.5	160	657.8	21.1	246
27-Jun-01	8.6	163	657.8	17.2	242
12-Jul-01	8.5	159	511.6	22.3	234
17-Jul-01	8.2	161	511.6	23.1	242
24-Jul-01	8.3	140	511.6	23.3	226
2-Aug-01	8.0	128	256.3	24.0	228
9-Aug-01	8.1	153	256.3	20.6	239
10-Aug-01	8.1	150	256.3	20.4	236
16-Aug-01	8.0	162	256.3	22.3	240
22-Aug-01	8.2	148	256.3	22.3	236
30-Aug-01	8.1	150	256.3	17.3	240