

Biogeochemical Contributions to the Water Quality of the Skeena River

by Solomon Henson

INTRODUCTION

The Skeena River watershed is about 54,000km² and extends from central British Columbia to the western coast (figure 1). The river is known for producing tremendous salmon fisheries. Slaymaker (1972) reported that the chemical quality of the Skeena River was high which provides an excellent environment for salmon populations to flourish despite heavy fishing pressures. The Skeena is a diverse watershed that receives water from glacial ablation, snow melt, and precipitation as rain. These hydrologic inputs transport ion species and sediment from the landscape to the river and determine what the overall water quality of the Skeena will be.

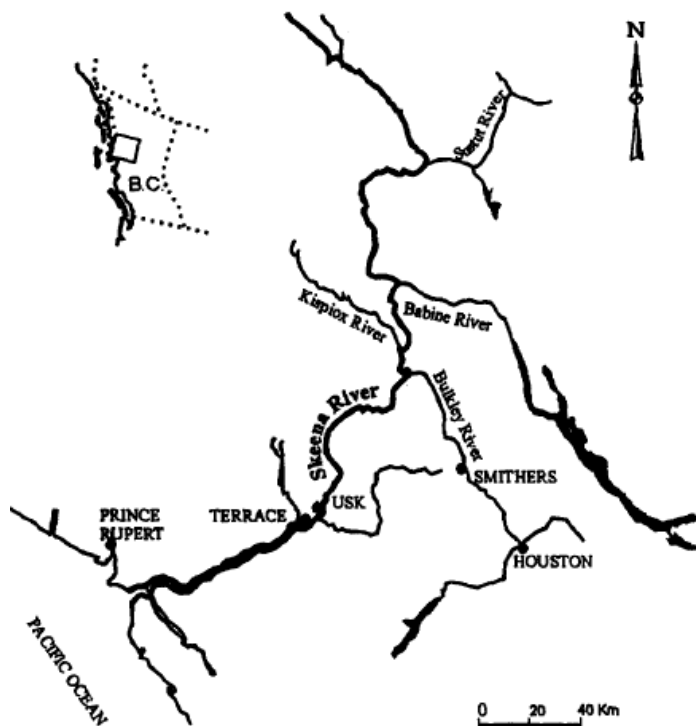


Figure 1. Skeena River basin showing location of settlements and major tributaries (Bhangu and Whitfield 1997).

There are three distinct types of tributaries on the Skeena that result from these hydrologic inputs. Those of glacial origin, those that flow clear and are derived from spring water, and those that are tea colored due to high levels of dissolved organic carbon and other organic material. Although the tributaries of the Skeena River have not been extensively studied, this paper will attempt to lay out the possible contributions of these waters to the overall water quality of the main stem. Furthermore, possible mechanisms for these contributions will be considered that include the effects of weathering, temperature, vegetation and soil type on water quality.

In 1977 Gibbs laid out three major mechanisms controlling worldwide water chemistry. Atmospheric precipitation dominates in tropical regions where nutrient and organic leaching are high, such that precipitation contains higher solute concentrations than the soil. Evaporation/crystallization processes dominate large river and lake systems that can be found in hot arid climates as well as in ocean water systems. And lastly, “rock dominance”, or the mineral content and weatherability of the landscape, controls the input of ions and sediment in lakes and streams in cold or temperate environments. We would expect the Skeena River chemical signature to be controlled by the geology of the region due to its cold, wet climate and high snow and glacial water contributions. However, the role of precipitation and evaporation/crystallization processes can still play unique and crucial roles in the development of rock-dominated systems as described by Hudson and Golding (1997).

GEOLOGIC CONTRIBUTIONS TO WATER QUALITY

The majority of the Skeena River lies within the intermontane belt. This belt is made of uplifted marine sedimentary rocks that are more conducive to weathering than either igneous or metamorphic rocks. In the downstream reaches, the Skeena River enters into the coastal belt that consists of granitic rocks (figure 2). These rock types are the parent materials from which different forms of weathering can occur. Chemical weathering occurs most often when ions such as carbonates, sulfates, silicates, sodium, magnesium, and potassium are hydrolyzed while in contact with water and are mobilized from the rock or soil to a watercourse. In general those minerals that contain iron, magnesium and calcium and minerals that have high oxygen to silica ratios (ie plagioclase feldspar and olivine) tend to weather more easily (Schlesinger, 1991).

Mechanical weathering is a physical process that can increase the rate of chemical weathering by increasing the surface area of parent rock minerals. Types of mechanical weathering include ice wedging, the breaking of rocks by root growth and by the movement of glaciers over the landscape.

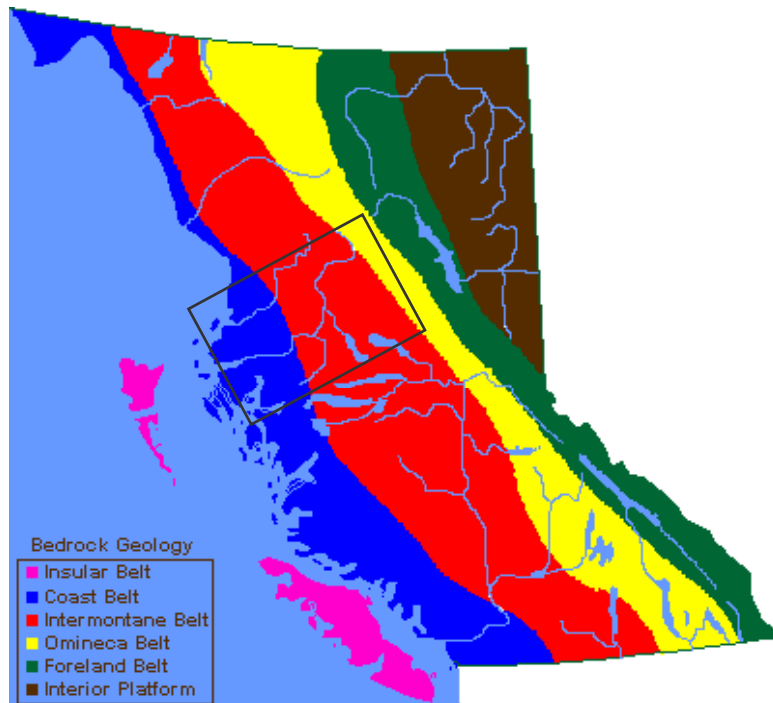


Figure 2. The geologic belts of British Columbia (Forseth, 1995).

Glacial Tributaries

The tributaries of the Skeena River that are fed by glaciers are generally characterized by highly turbid waters. This is a result of ice flows crushing and grinding the rock material into a powder. In experimental studies Brown (1996) determined that “rock flour,” due to its decreased particle size and increased water mineral contact, should allow for greater releases of solutes into solution in natural systems. These glacial streams often have elevated turbidity levels, and the sediment that is flushed into stream and river systems has minerals exposed at the surface that can be hydrolyzed. Figure 3 shows a highly turbid stream fed by glaciers in New Zealand.



Figure 3. Turbid glacial waters on South Island in New Zealand (Greenspun, 1992).

Studies by Edwards (2000) in Alaska compared the relative turbidity rates and solute concentrations of clear water and glacial streams on both igneous and sedimentary rock material. She found that glacial streams in both igneous and sedimentary rock settings had elevated turbidity levels compared to those of clear water streams. She also discovered that glacial streams in the sedimentary rock setting had elevated solute concentrations compared to clear water streams. These are results that we would expect to find in the Skeena drainage based on Brown's dissolution kinetics discoveries. However, she found that solute concentrations were higher in clear water streams than in glacial streams in the igneous rock setting (see figure 4). These results did not match the conclusions of dissolution kinetics laid out by Brown, which found that glacial grinding of rock material increased the level of solutes in the system. Another explanation of these results could be that because igneous rocks are more resistant to chemical weathering and the mechanical weathering of glaciers, they contribute lower solute concentrations. These lower concentrations could be masked by groundwater inputs of solutes into the glacial water stream. Due to the fact that clear water systems have higher groundwater

concentrations than glacial systems, we would expect to see the results that Edwards determined. Overall, we would expect the glacial tributaries of the Skeena River to produce high dissolved ion concentrations as well as high turbidity and suspended solids, because the watershed predominantly consists of sedimentary rock. Contributions of solutes from the granitic coast range, however, may be dominated by groundwater systems rather than glacial processes.

	Sedimentary	Igneous
Clear water	Turbidity = 21.5 NTU TDS = 239 mg /l	Turbidity = 15 NTU TDS = 50.72 mg /l
Glacial Water	Turbidity = 258 NTU TDS = 363 mg /l	Turbidity = 79 NTU TDS = 21.3 mg /l

Figure 4. Edwards (2000)

Spring Fed Contributions to Water Quality

Drivers of groundwater chemistry are necessary to consider when determining water chemistry inputs from rainfall and snow melt. Hudson and Golding (1997) found that major contributors to the weathering of soils were dependent on the hydraulic conductivity of the soil, the temperature of the region, and vegetation cover. They found that as hydraulic conductivity increased the concentration of ions decreased in the soil. If hydraulic conductivity was high, there was a constant flushing causing continuous chemical weathering of the soil. This led to high denudation rates of cations and anions, but because the flow of water was high through the soil, the concentration of these ions was diluted. If the hydraulic conductivity was low, there was a longer residence time leading to a greater build up of chemically weathered ions in the soil before the solution was discharged into the stream. This result has been a reoccurring theme in groundwater studies and has been heavily supported (Denning et al., 1992; Hendershot et al., 1992). These results are also supported by Skeena River water quality data, which exhibits a strong diluting signal for dissolved solutes during snow melt events in May and June when hydraulic conductivity and discharge is high. Figure 5 displays the sodium signature for the

Skeena River over one year. This pattern is typical of solutes in the Skeena River where solutes plummet at the onset of high discharges in the spring and throughout the summer. During the period between late fall and early spring, discharge is lowest and solute concentrations are at their peak due to higher residence times of water within the soil (Bhangu and Whitfield, 1997).

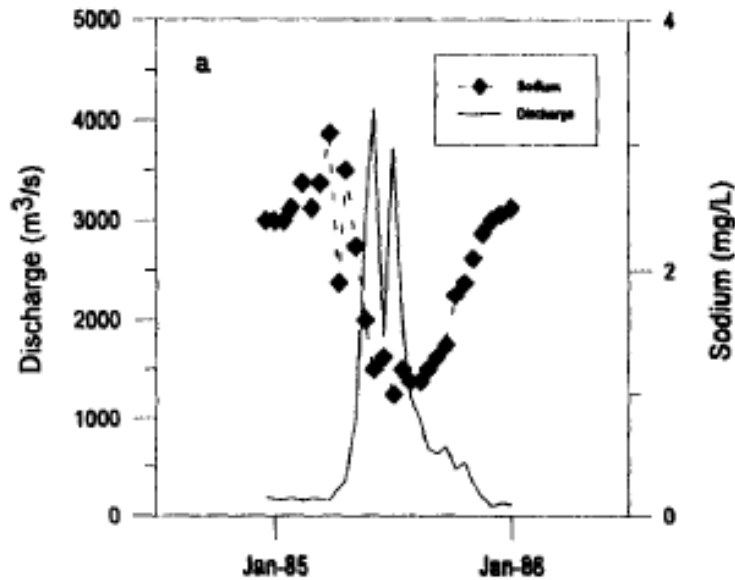


Figure 5. Bhangu and Whitfield (1997)

Figure 6 displays the solute to discharge relationship with respect to the type of site that was analyzed. At hillside sites where hydraulic conductivity was highest, the lowest ion concentrations were observed, and at streamside sites where gravitational influences were lowest, there were higher residence times and thus higher solute concentrations. Thus, we can clearly see that higher discharge rates lead to a diluting of solutes and that local landscape types (hillside and streamside sites) control discharge rates.

Figure 6 also summarizes how vegetation can affect the water chemistry contributions to a watershed. As vegetation cover diminished, higher contributions of solutes were observed. The exceptions to these patterns were nitrate, chloride, ammonium, and sulfate. These species were found to be in higher concentrations in precipitation than in groundwater. Thus, these systems are possibly influenced more by atmospheric contributions than they are controlled by groundwater. Hudson and Golding hypothesized that thick vegetation canopies block irradiance

and in doing so reduce the temperature of a given site. It was noted by Riebe et. al. (2003) and others that chemical weathering increased in intensity as the average temperature increased. Based on these findings, Hudson and Golding, felt strongly that the reduction of temperature due to vegetation cover reduced the available solutes in the soil that contributed to water chemistry. Spring-fed streams are controlled by soil processes and soil- water interactions. Thus, in order to analyze groundwater contributions of water quality in the Skeena watershed, one must take into account landscape geometry, vegetation cover, and climate.

Parameter	Mature Lodgepole pine		Mature spruce-fir		Immature spruce-fir-pine	
	hillside	streamside	hillside	streamside	hillside	streamside
NO ₃	0.77 (1.53)	0.99 (1.15)	1.11 (2.76)	2.24 (3.10)	1.37 (2.51)	14.6 (21.8)
Cl	20.4 (18.7)	29.5 (18.9)	11.2 (10.2)	13.9 (11.8)	13.3 (11.9)	15.4 (10.8)
SO ₄	10.2 (3.0)	10.8 (5.4)	7.27 (2.39)	11.0 (4.4)	5.21 (2.77)	6.76 (2.39)
HCO ₃	175.3 (53.1)	191.0 (66.6)	143.7 (9.6)	172.5 (65.3)	260.8 (23.7)	235.7 (29.5)
NH ₄	3.14 (5.52)	3.16 (4.40)	0.88 (1.39)	1.39 (1.94)	1.04 (1.16)	0.89 (1.74)
Ca	57.9 (24.5)	51.2 (18.6)	35.9 (4.1)	47.0 (34.3)	74.9 (12.5)	69.6 (12.4)
Mg	10.4 (3.2)	17.8 (5.2)	6.22 (0.75)	8.23 (2.34)	17.0 (1.9)	23.1 (3.5)
K	12.1 (5.4)	27.1 (17.6)	7.07 (1.60)	7.74 (2.93)	12.9 (3.6)	9.72 (3.45)
Na	65.2 (26.9)	95.8 (52.8)	62.2 (20.4)	77.4 (23.2)	88.7 (23.5)	91.9 (24.5)
SiO ₂	160.7 (17.1)	169.3 (23.3)	155.7 (16.7)	149.1 (27.1)	174.7 (24.0)	164.0 (28.2)
H ⁺	0.44 (0.22)	0.45 (0.21)	0.51 (0.16)	0.52 (0.36)	0.29 (0.09)	0.28 (0.10)
K (m/s)	2.28 × 10 ⁻⁶	1.95 × 10 ⁻⁶	7.90 × 10 ⁻⁷	1.30 × 10 ⁻⁶	1.10 × 10 ⁻⁵	5.60 × 10 ⁻⁶

All concentrations are in $\mu\text{mol/l}$. The values in parentheses are standard deviations.

Figure 6. Hudson and Golding (1992)

Tributaries with Elevated Organic Carbon

For stream and riverine systems, carbon input is most commonly derived from allochthonous material, such as leaves and branches falling into the watercourse, or from the leaching of dissolved organic carbon (DOC) from soils adjacent to the watercourse. Those streams that are “tea colored” on the Skeena River are possibly fed by soils that are rich in organic carbon. It has been shown by Chapmann et. al (2001) that soil cores taken in vegetated regions had a much greater leaching rate of DOC than those in un-vegetated regions. Once leaves and plant material fall to the forest floor, they begin to degrade with the assistance of microorganisms and become incorporated into the soil as organic carbon. Andersson and

Nilsson (2001) describe how microorganisms will degrade leaves and plant material at accelerated rates under conditions of high temperature and high lime content (high pH). These conditions lead to high DOC levels in the soils, but whether or not these soils can readily release this organic carbon is a complex dynamic. Studies have shown that DOC leaching can depend on the type of vegetation, the pH of the soil, the soil type, and the amount of organic carbon stored in the soil (Chapman et al 2001, Andersson et al 1994, Kahle et al 2003).

The organic rich tributaries of the Skeena River may also be fed by peat fens, otherwise known as sphagnum fens. Peat fens are wetlands that are commonly found in wet and cold climates (like British Columbia) due to their inability to withstand dry summer months. The most telling characteristic of a peat fen is that the degradation of plant material is slower than the growth rate. Sphagnum is the most common plant found in peat fens and bogs (figure 7). When these plants die the next generation of sphagnum grows on top, eventually (sometimes over thousands of years) creating a thick layer of dead material below the growth layer. This dead layer is known as peat. Thus, Sphagnum will steadily accumulate peat at rates between 3 and 28mm per year (Ohlsen and Oakland, 1998). Sphagnum assists the accumulation process by secreting organic acids into its environment so that very few plants can survive in the fen and bacterial growth and the ability of microorganisms to degrade plant material is inhibited (Mitsch and Gosselink p449). As a peat fen reaches maturity, a tremendous amount of organic carbon has built up in the decaying layers; some scientists have estimated that peat lands store up to 33% of the world's carbon. This endless supply of carbon can be leached from the peat fens at very high concentrations and may be the source of the Skeena River's DOC rich streams.



Figure 7. Photograph of Sphagnum (Kaczarowska 2003).

SEASONALITY OF SKEENA WATER CHEMISTRY

The Skeena River has two distinct flushing events, one in early summer between May and June and the other in late summer between October and September (figure 8). The first high discharge event is due to warming temperatures and melting of the seasonal snow-pack, and the second is based on early season rainfall. Contributing to these discharge events is glacial meltwater. These events are characterized by their own unique water quality signature that helps determine which processes are the major water quality drivers at different times of the year for the Skeena River. Bhangu and Whitfield (1997) plotted discharge of the river versus concentration in order to characterize the seasonal water quality of the Skeena River. These plots, known as hysteresis plots, show where the maximum or minimum concentration of a water quality species falls in relationship to peak discharge (figure 9). If the concentration peak occurs before peak discharge, the hysteresis plot displays a clockwise loop; if the concentration peak occurs after peak discharge, the hysteresis plot displays a counterclockwise loop; and if the concentration is linearly related to discharge no loop will form. The hysteresis plot also displays whether or not water quality species have positive or negative relationship to discharge.

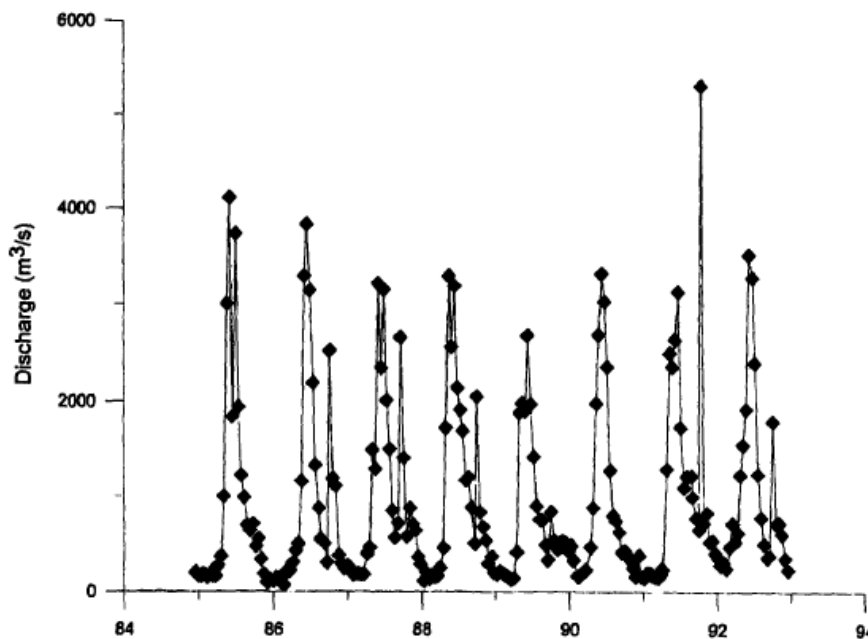


Figure 8. Hydrograph of the Skeena River from 1985 to 1993 (Bhangu and Whitfield 1997).

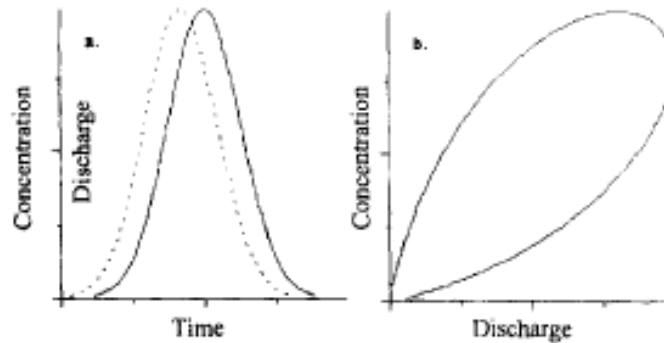


Figure 9. Time-series plot (a) and hysteresis plot (b) for a variable out of phase with discharge (Bhangu and Whitfield 1997).

Based on the hysteresis plots, Bhangu and Whitfield found that cations and anions were inversely related to discharge and exhibited a clockwise hysteresis. This means that the minimum concentration of these species occurred before the peak discharge of the season, probably due to the groundwater dilution of these species based on snow melt. As discharge increases in early summer, ions are immediately flushed from the soil particles leading to early concentration peaks. By the time peak discharge occurs, the water entering the streams is fairly dilute.

Iron, turbidity, phosphorus, and zinc had a positive relationship to discharge. This relationship is caused by erosion of sediments as water flows over the landscape with enough velocity to dislodge sediment particles from the soil. Due to the high binding affinity of soils to phosphorus, zinc, and iron, these constituents would likely mirror the relationship between turbidity and discharge. Because complexes of soil particles and related species are pulled into suspension by erosion, we would expect to see a linear relationship between discharge and turbidity and a flat hysteresis (no loop) diagram if the system were based on rainfall. However, the hysteresis loop for the Skeena River is open and runs clockwise. This indicates that either snow melt or glacial melt, not rainfall, is probably the driver of turbidity and turbidity related species in the Skeena River.

Further studies by Whitfield and Clark (1992) in snow melt dominated systems in the Rocky Mountains in British Columbia found that hysteresis loops were very flat and looped counterclockwise. Thus concentration peaks were occurring at or after peak discharge. These results also do not match the Skeena River pattern. Therefore, we would expect that glacial

systems play a major role in controlling the turbidity and turbidity related water quality species for the Skeena River, whereas snowmelt may be the dominant driver for solute related water quality species. As stated earlier, glaciers create rock flour as they move across the landscape. During glacial melt periods the sediment particles can immediately be suspended in solution and can contribute to the overall water chemistry before peak glacial discharges are attained.

Bhangu and Whitfield (1997) found that sulfate, nitrate and nitrite concentrations were anomalous with respect to the other ions measured in the Skeena River. Sulfate displayed an unexpected counterclockwise pattern in the hysteresis diagram. Studies by Hudson and Golding (1997) in southern British Columbia determined that the major source of sulfate was contributed by the atmosphere. This may be a reason for the anomalous patterns. Nitrate and nitrite water quality patterns are less mysterious. Due to the tremendous amount of nitrogen controlled by biological processes, we would expect seasonal nitrate patterns to follow growth and degradation cycles of plants, algae, zooplankton, macroinvertebrates and fish.

CONCLUSION

The inputs on the main stem of the Skeena River are in large part controlled by inflowing tributaries. These tributaries are fed by turbid glacial meltwater, groundwater aquifers replenished by snowmelt, or wetlands. Based on these hydrologic flowpath regimes, each basin carries its own chemical signature, and the geology of the basin determines which constituents are available for mobilization. As the Skeena River flows down through the intermontane belt, it may pick up the highly turbid flows of glacial meltwater from one source, and then be diluted by a large clean flowing snowmelt tributary from the next. The timing of the tributary contributions is an ever-present force creating strong yearly patterns in water chemistry. In the winter months the Skeena River runs clear, while the spring months are characterized by high discharge and may have high turbidity due to glacial meltwater. These yearly chemical patterns shape and interact with the biological community determining size and quality of algal, bacterial, and fish populations and providing seasonal cues for fish migration and spawning. Biotic populations add the final layer of complexity to the biogeochemical cycle of nutrients and other solutes as organisms grow, die, and degrade. The water quality of the Skeena River is intricate and highly

complex, but it provides a crucial foundation for understanding how the health of the ecosystem is maintained.

REFERENCES

- Andersson S. and Nilsson S.I. 2001. Influence of pH and temperature on microbial activity, substrate availability of soil-solution bacteria and leaching of dissolved organic carbon in mor humus. *Soil Biology and Biochemistry* 33(9): 1181-1191.
- Andersson S., Valeur I. and Nilsson I. 1994. Influence of lime on soil respiration, leaching of DOC, and C/S relationships in the mor humus of a haplic podsol. *Environment International* 20(1): 81-88.
- Bhangu I. and Whitfield P.H. 1997. Seasonal and long-term variations in water quality of the Skeena river at Usk, British Columbia. *Water Research* 31(9): 2187-2194 .
- Brown, G. H., Tranter M., et al. 1996. Experimental Investigations of the Weathering of Suspended Sediment by Alpine Glacial Meltwater. *Hydrological Processes* 10(4): 579-597.
- Chapman P.J., Williams B.L., and Hawkins A. 2001. Influence of temperature and vegetation cover on soluble inorganic and organic nitrogen in a spodosol. *Soil Biology and Biochemistry* 33 (7-8): 1113-1121.
- Denning, A.S., Baron, J., Mast, M.A., and Arthur, M. 1992. Hydrological pathways and chemical composition of runoff during snowmelt in Loch Vale Watershed, Rocky Mountain National Park, Colorado, USA. *Water Air and Soil Pollution* 59: 107-123.
- Edwards, P., Tranel M., et al. 2000. Stream and river water quality in Denali National Park and Preserve, Alaska. Proceedings; AWRA's spring specialty conference; Water resources in extreme environments. D. L. Kane. Bethesda, AWRA - American Water Resources Association: 203-207.
- Forseth A. 1995. www.bcadventure.com/adventure/frontier/physio/geology.htm. Date accessed 5-15-04.
- Gibbs, R.J. 1970. Mechanisms controlling world water chemistry. *Science* 170: 1088-1090.
- Greenspun P. 1992. <http://www.photo.net/photo/pcd1645/glacier-walk-looking-back-54>. Date accessed 5-15-04.
- Hendershot, W.H., Mendes, L., Lalonde, H., Courchesne, F., and Savoie, S. 1992. Soil and stream water chemistry during spring snowmelt. *Nordic Hydrology* 23: 13-26.

- Hudson, R.O. and Golding, D.L. 1997. Controls on groundwater chemistry in subalpine catchments in the southern interior of British Columbia. *Journal of Hydrology* 201: 1-20.
- Kaczarowska M. 2003. http://india.ipj.gov.pl/pars_septima/las/sph1.jpg. Date accessed 5-20-04.
- Kahle M., Kleber M., and Jahn R. 2003. Retention of dissolved organic matter by illitic soils and clay fractions: Influence of mineral phase properties. *Journal of Plant Nutrition and Soil Science* 166(6): 737-741.
- Mitsch, W.J. and Gosselink, J.G. 2000. Wetlands. 3rd edition. Van Nostrand Reinhold, New York.
- Ohlson M. and Okland R.H. 1998. Spatial variation in rates of carbon and nitrogen accumulation in a boreal bog. *Ecology* 79 (8): 2745-2758.
- Riebe C.S., Kirchner J.W., and Finkel R.C. 2003. Long-term rates of chemical weathering and physical erosion from cosmogenic nuclides and geochemical mass balance. *Geochimica et Cosmochimica ACTA* 67 (22), 4411-4427.
- Schlesinger W.H. 1991. Biogeochemistry: An Analysis of Global Change. Academic Press. San Diego, Ca.
- Slaymaker H.O. 1972. Physiography and hydrology of six river basins (Edited by Robinson J. L.). *Geography of British Columbia*: 32-68.
- Whitfield P.H. and Clark M.J.R. 1992. Patterns of water quality in the Rocky Mountains of British Columbia. In: *Science and the Management of Protected Areas*, pp. 391--409.