Assessment of Water-Rock Interactions in the Upper Bow River Basin using Chemical and Isotopic Parameters for Surface Water and Groundwater Samples

S.K. Provencher
University of Calgary, Calgary AB
skproven@ucalgary.ca

and

S. Grasby and B. Mayer
Geological Survey of Canada, Calgary AB
University of Calgary, Calgary AB

Summary
Knowledge of basin geology, its effects on groundwater, and the influence of groundwater-surface water interactions can be used to explain chemical and isotopic variability in rivers fed largely by groundwater. In this paper, geological controls on the natural chemical variability within the Upper Bow River were defined using chemical and isotopic data of groundwater, surface water and rock-water interactions with possible rock types. Groundwater samples were studied and 3 water types were defined: Ca-Mg-HCO_3, Na-HCO_3 and Ca-Mg-Na-HCO_3-Cl. The latter was due to the addition of NaCl to the system and mixing with Ca-Mg-HCO_3 waters which correlates with well locations situated near major roads, suggesting the presence of road salt. Ca-Mg-HCO_3 waters result from dissolution of limestone and dolomite rocks which are abundant within the Cambrian and Devonian carbonates which underlie much of the basin. Na-HCO_3 waters were present in only 2% of the samples and result from the dissolution of shale and sandstone units which are present within the Mississippian and Cretaceous siliciclastics. Ca-Mg-HCO_3, the water type in all 13 surface water samples was similar to 93% of the groundwater samples. Also, $\delta_{18}O$ and δ_2H water isotope values in groundwater and surface water samples were consistent, indicating strong surface water-groundwater interaction. $\delta_{18}O_{(BaSO4)}$ results were indicative of sulphur reduction, suggesting surface water first travelled through anoxic groundwater pathways before being discharged as surface water. Surface water $\delta_{13}C$ values in Dissolved Inorganic Carbon (DIC) were found to be sourced from soil zone and carbonate rock weathering which agrees with previous work in the area (Grasby, 1997). Surface water $\delta_{34}S$ values were variable, suggesting multiple sulphur sources. The negative and low positive values were representative of pyrite oxidation, a process known to occur in the Exshaw unit found within the basin (Caplan and Bustin, 2001). The highly positive values suggest gypsum dissolution possibly within the gypsum rich Devonian carbonates.

Introduction
The study of both groundwater and surface water quality is of growing importance worldwide, especially in regions like the Bow River Basin - the most populated river basin in Alberta. With populations still rising, and no surface water allocation rights currently available, the Bow River has been deemed one of the most water stressed regions in Canada (Turner et al., 2005). The source of water in the Bow River is 20% rain, groundwater and glacier melt and 80% snowmelt (Turner et al., 2005). Most of this water is sourced from the headwater regions in the Rocky Mountains, where the mountain chain forces air to rise and cool, causing moisture to condense and fall as rain or snow. The rain out experienced in the mountains leaves little moisture for the prairies, creating a rain shadow (Turner et al., 2005). Understanding what processes are influencing water as it travels from the source area in the mountains and is discharged into the Bow River will aid in understanding any possible controls on the chemistry of the river itself.

Grasby (1997) demonstrates that groundwater heavily influences the hydrodynamics of the river. In fall and winter the discharge is predominantly baseflow derived (fed by groundwater) due to seasonal cold and dry conditions. In contrast during the spring season discharge is comprised of both rainfall and groundwater, and in the summer discharge is fed predominantly by rainfall. Interestingly, the chemistries remain constant throughout the year despite varying sources, suggesting that rainwater must travel through groundwater pathways before it is discharged into the river (Grasby, 1997). Therefore, further investigation into factors affecting groundwater chemistry within this region would contribute to a better understanding of the possible sources of natural variability in the Bow River itself. A geochemical study of the Upper Bow River was undertaken to investigate the extent to which groundwater chemistry is controlled by rock-water interactions within the basin, and if these processes are in turn controlling the water chemistry within the Upper Bow River. The study area focuses on the headwaters region where the river receives most of its water through rainout in the Rocky Mountains. Understanding what processes are influencing water as it travels from the source area in the mountains and is discharged into the Bow River will aid in understanding any possible controls on the chemistry of the river.

There have been relatively few studies of the chemistry and water quality of the Bow River considering the reliance on the river to support a large population. Grasby (1997) studied the chemistry of the Bow River through geochemical means using stable isotopes, and utilized the study of major ions and the carbon cycle to help characterize the variable geochemical and hydrogeological aspects of the river. In his paper, the variability and spatial distribution of water types was well outlined, but further study of the basin geology and plausible water types that can be formed with dissolution of these units can give insight into what rock types have a greater impact on the chemistry of the Bow River. Grasby and Hutcheon (2000) demonstrate how weathering of the carbonate basin in the Bow River Valley leads to specific water chemistries seen in surface waters, and surface water chemistries were used to calculate weathering rates of the carbonate basin. Grasby et al. (1999) also studied the interaction of surface water and groundwater of the Bow River and its effects on water chemistry. They explain how major ion chemistry in rivers is largely dependent on rock water interactions. McFarland (1997) studied possible subsurface controls on water quality in the Stoney Indian Reserve located in Morley, AB, just east of the proposed study area. Surface water chemistry was examined to determine the nature of the subsurface geology. It was deduced that surface water chemistries could be correlated with certain rock types and that weathering of these rocks proved to be a possible control on the ionic composition of the water. Manwell (2005) studied the relationship between surface water - groundwater interaction and its effects on water quality of the Elbow River. It was shown that in certain instances groundwater can greatly influence the water quality of surface water. Various other studies researched the effects of different lithologies on water chemistry with emphasis on rock-water interactions and weathering processes (Frape et al., 1984; Bluth and Klump, 1994; Norstrom et al. 1984).

Methodology

Using methods and theories presented in the above articles, further research can be conducted to provide more information on possible rock types within the basin which may influence the natural water chemistry variability within the Upper Bow River Basin. To achieve this, an understanding of the basin geology and both groundwater and surface water chemistry and interaction is imperative. The Upper Bow River basin is dominated by Cambrian and Devonian carbonates. Cambrian carbonates were deposited in an open marine setting, whereas Devonian carbonates were deposited in a restricted marine setting, which leads to development of evaporite minerals (Mossop and Shetsen, 1994). From Lake Louise to Banff, the area is underlain dominantly by Cambrian carbonates interbedded with calcareous shales (Mossop and

Shetsen, 1994). From Banff towards Seebe, Devonian carbonates are dominant. Further west, towards Calgary is largely underlain by Cretaceous to Paleocene sandstones and shales. The majority of the river valley is overlain by glacial till. The till consists of rocks which are carbonate, metamorphic and igneous in origin (Clark, 1949; Moran, 1986). Groundwater data was obtained from Alberta Environment, and 63 wells with complete major ionic chemistry analyses were studied. Ca^{2+}, Na^{+}, K^{+}, Mg^{2+}, SO_4^{2-}, NO_3^{-}, HCO_3^{-} and Cl^{-} concentrations along with available stable isotope data consisting of $\delta_{18}O$, and $\delta_{2}H$ were the focus of the groundwater geochemical analysis. Surface water data was obtained during fall of 2009, by sampling 13 major tributaries which drain into the Bow River from Canmore, west to Exshaw and south to Kananaskis. Major ion and stable isotope analyses were conducted as stated above with the additional analysis of $\delta_{13}C$ in DIC, and $\delta_{34}S$. These results were compared against those obtained from the groundwater analysis. A comparison of groundwater and surface water results was used to identify the extent to which groundwater influences surface water chemistry.

Examples

Through analysis of the groundwater data, 3 major water types were identified: Ca-Mg-HCO_3, Na-HCO_3, and Ca-Mg-Na-HCO_3-Cl. The latter was due to the addition of NaCl to the system and mixing with Ca-Mg-HCO_3 waters. These wells were all located on major roads, suggesting the addition of NaCl was due to the presence of road salt. 93% of the wells were Ca-Mg-HCO_3 waters resulting from dissolution of limestone and dolomite rocks which are abundant within the Cambrian and Devonian carbonates that underlie much of the basin from Lake Louise to Calgary. 2% of the groundwater sample had a water type of Na-HCO_3, indicating dissolution of sodium rich sandstones or shales, which are present within the Mississippian and Cretaceous siliciclastics west of Seebe (McFarland, 1997). Ca-Mg-HCO3 was shown to be the water type in all 13 surface water samples. $\delta_{13}C$ values in DIC ranged from -10.93 to -6.78‰ in the surface water samples. Grasby (1997) demonstrated that $\delta_{13}C$ values within the Bow River sourced from soil zone and carbonate rock weathering would range from -7 to -12‰ during fall, where the river is largely fed by groundwater. This is consistent with the observed values in the surface water samples. δ34S values in the surface water samples ranged from -5.44 to 20.36‰. This large variation is likely due to differing sources of sulphur. The negative and low positive values are indicative of pyrite oxidation (Andre *et al,* 2005). Pyrite is present in shales within the Exshaw unit of the Mississippian. The more positive values are characteristic of gypsum dissolution, which is readily available within the Devonian carbonates. $\delta_{18}O$ and $\delta_{2}H$ water values ranged from -17.17 to -26.35‰ and -136.47 to -157.78‰ respectively in the groundwater samples. In the surface water samples $\delta_{18}O$ and $\delta_{2}H$ values ranged from -19.04 to -19.99‰ and -145.11 to -151.95‰ respectively. The smaller variation in the surface water isotopes is likely due to a higher degree of mixing. The similar water isotope values obtained from the surface and groundwater data is indicative of strong groundwater-surface water interaction. This is consistent given that the surface water samples were taken in the fall, where surface water is largely fed by groundwater (Grasby, 1997).

Conclusions

The population of a large geographic area relies on the Bow River to support agriculture, industry and domestic uses. Therefore, understanding influences that affect the natural chemical variability of the river is of great importance. This paper outlines the geological controls influencing groundwater and ultimately surface water feeding into the Bow River. It was shown that a clear knowledge of the basin geology, its effects on groundwater, and the influence of groundwater-surface water interactions, can be used to explain observed natural variability in rivers which are largely fed by groundwater. This information can be used in further studies to establish relative residence times within certain rock types and even geologic units, which would be beneficial in future studies to construct potential flow paths for water recharging the Bow River.

Acknowledgements

I'd like to thank Dr. Steve Grasby for his encouragement and support throughout my research and my time at the GSC. Also to Dr. Bernhard Mayer and the Applied Geochemistry Group for their support and help which enabled me to finish this project. I'd like to thank Gennyne McCune for her editing expertise and ongoing emotional support. Lastly I'd like to thank Sean Assie for being a remarkable field assistant.

References

Andre, L., Franceschi, P., Pouchan, P., and Atteia, O., 2005, Using geochemical data andmodelling to enhance the understanding of groundwater flow in a regional deep aquifer, Aquitaine Basin, south-west of France: Journal of Hydrology*,* 33, 50-62.

Bluth, G.J.S., and Klump, L.R., 1994, Lithologic and climatologic controls of river chemistry. *Geochimica et Cosmochhica Acta*, 58, 2341-2359.

Caplan, M.L., and Bustin, R.M., 2001, Paleoenvironmental and plaeoceanographic controls on black, laminated mudrock deposition: example from Devonian-Carboniferous strata Alberta, Canada: Sedimentary Geology, 145, 45-72.

Clark, L.M., 1949, Geology of Rocky Mountain front ranges near Bow River, AB: AAPG Bulletin, 33.

Frape, S.K., Fritz, P., and McNutt, R.H., 1984, Water- rock interaction and chemistry of groundwaters from the Canadian Shield. Geochimica et Cosmochimica Acta, 48, 1617-1627.

Grasby, S.E., 1997, Controls on the chemistry of the Bow River, Southern Alberta, Canada: PhD Thesis, University of Calgary, Calgary, 1-140.

Grasby, S.E., and Hutcheon, I., 2000, Chemical dynamics and weathering rates of a carbonate basin Bow River, southern Alberta: Applied Geochemistry, 15, 67–77.

Grasby, S.E., Hutcheon, I., and McFarland, L., 1999, Surface-water–groundwater interaction and the influence of ion exchange reactions on river chemistry: Geology*,* 27, 223–226.

McFarland, L.M., 1997, Using the chemical and isotopic characteristics of drinking water to determine sources of potable water and subsurface geologic controls on water chemistry, Stoney Indian Reserve, Morley, AB: Master's Thesis, University of Calgary, Calgary, AB. 1-115.

Manwell, B. R., 2005, Groundwater – surface water interaction and water quality in theLower Elbow River, Alberta. Master's Thesis. University of Calgary. Calgary, AB.

Moran, S.R., (1986) Surficial geology of the Calgary urban area: Alberta Research Council, Terrain Sciences Department.

Mossop, G.D., and Shetsen,I., 1994, Geological atlas of the Western Canada Sedimentary Basin: Canadian Society of Petroluem Geologists and Alberta Research Council, 223-230.

Nordstrom, D.K., Ball, J., Donahoe, R.J., and Whittemore, D., 1989, Groundwater chemistry and water rock interactions at Stripa: Geochimica et Cosmochimica Acta*,* 53, 1727-1740.