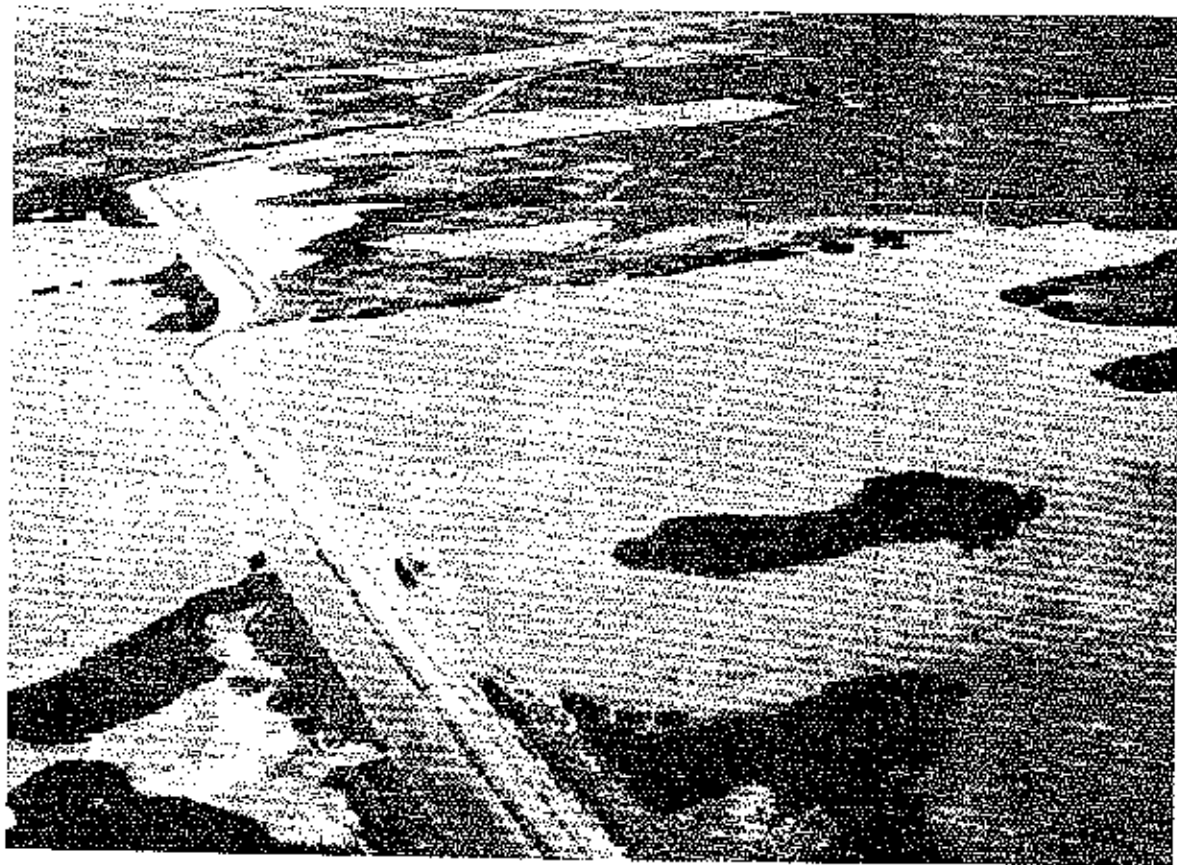


Canadian Water Resources Journal

Vol. 15, No. 4, Winter/hiver, 1990

Revue canadienne des ressources hydriques



CANADIAN WATER RESOURCES ASSOCIATION
L'ASSOCIATION DES RESSOURCES HYDRIQUES

GROUNDWATER CONTRIBUTION TO ACID DRAINAGE FROM THE HALIFAX FORMATION IN NOVA SCOTIA

Submitted June 1989; accepted September 1990

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Abstract

Acid drainage from disturbance of the Halifax Formation is common in Nova Scotia due to the pyritic nature of this bedrock. This paper documents an investigation of the role of groundwater into the production and transport of acid drainage from a quarry in the Halifax Formation. The results have implications for remediation of existing acid drainage sites as well as for managing developing quarries such that acid drainage is minimized. It is concluded that excavation below the groundwater table accelerates the rate of acid generation at the surface. Iron and sulphate were found to be relatively mobile in groundwater while aluminum and acidity were found to be relatively immobile.

Résumé

Le drainage acide, résultat du dérangement de la "formation Halifax", est commun en Nouvelle-Ecosse. Ce rapport documentaire décrit une investigation du rôle de l'eau sous-terrainne dans la production et le transport du drainage acide. Cette étude a été entreprise dans une carrière de la "formation Halifax". Les résultats identifient des implications afin de remédier les sites de drainage acide en existence, et afin de développer des carrières qui minimisent le drainage acide. Enfin, on conclut que les fouilles sous la nappe d'eau accélèrent la vitesse de la production d'acide sur la surface de la terre. Le fer et le sulfate sont relativement mobiles dans l'eau sous-terrainne tandis que l'aluminium et l'acidité sont relativement stables.

Introduction

In Nova Scotia it has been recognized for several years that severe water quality impairment can occur when bedrock of the Halifax formation is disturbed. Drainage from such disturbances is characterized by very low pH and elevated metals concentrations. The potential for widespread water quality impairment by disturbance of the Halifax Formation is highlighted by the fact that the formation underlies approximately ten percent of the southern half of the province.

Slates of the formation possess a well-defined cleavage and are easily exca-

vated. Therefore, small borrow pits proliferate in rural areas as does the use of the material in roadbed construction. The pits and roads in some rural areas represent a potential network for input of acid drainage to the environment. King (1985) took 17 samples of surface runoff and standing water in a selection of 10 quarries and pits in the Halifax Formation. Samples generally exhibited elevated metals concentrations and low pH. Iron concentrations ranged from 0.24 to 120 mg/L, aluminum 1.1 to 47 mg/L and pH 2.6 to 4.2.

King (1987) supported earlier work by

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the Environmental Protection Service of Environment Canada (unpublished) which suggested that the quarry discussed in this paper was a major source of acid drainage to downstream waterways. King (1987) also found that the adjacent highway, built with material from the quarry, contributed as much acid drainage as the quarry.

Other types of construction activities have also generated acid drainage from Halifax Formation slates. The earliest and best documented case is that at the Halifax International Airport. The Airport is located on a topographic high separating two major watersheds: the Shubenacadie River and the Salmon River.

Scott (1981) attributed a major fish kill in the Shubenacadie River to construction activity in slate. The Environmental Protection Service (1976) attributed several fish kills in the river, between 1957 and 1976, to acid drainage caused by construction activity at the airport. Airport construction has also led to periodic disruption of water supplies for the towns of Elmsdale, Lantz and Enfield, which draw water from the river (Thompson, 1978).

Porter-Dillon (1985) suggested that fish in the Salmon River system were highly stressed by acid drainage from the airport runway drainage system and drainage from a large slate refuse pile on the airport property.

Lund *et al.* (1987), studied the role played by groundwater in acid drainage at the airport site. They reported that groundwater quality in disturbed bedrock has been dramatically impaired by acid generation. For example, groundwater samples drawn from disturbed areas yielded iron concentrations ranging from 344 to 2220 mg/L, aluminum from 128 to 445 mg/L and pH values from 3.25 to 3.75. Meanwhile, groundwater samples from undisturbed bedrock in the area showed iron concentrations from 0.12 to 0.32 mg/L, aluminum concentrations of less than 0.01 mg/L and pH values of 7.7. The authors also state that a significant portion of the acid drainage from the site bypasses an on-site treatment plant via groundwater flow.

Aside from the airport, studies of acid

drainage in Nova Scotia have focused only on surface waters as receiving and transport media. The effect of widespread quarrying of Halifax Formation bedrock on groundwater quality is unknown, as is the role of groundwater in the transport of acid drainage from quarries.

In 1985 a study was initiated, through funding by the Environmental Protection Service and the Natural Sciences and Engineering Research Council, to assess acid and metal loadings from two adjacent quarries in the Halifax Formation near the Halifax International Airport. One of the purposes of the work was to understand the role played by groundwater in acid generation and drainage from acid-producing quarries in this formation. The results would have implications with respect to remediation of acid drainage from existing quarries and evaluation of potential environmental impact from proposed quarrying or construction. This paper deals with the groundwater portion of the study.

Data on water entering and leaving the quarries was used to (a) determine the contribution of groundwater to the quality of surface drainage from one of the quarries and (b) investigate the movement, in groundwater, of the moieties of acid drainage.

The data collected included:

- the quantity and chemistry of surface water entering the quarry,
- groundwater chemistry and levels, and
- the quantity and chemistry of surface water exiting the quarry.

Methodology

Study Site

The study site is a 4.5 ha quarry known as the "west quarry". It is adjacent to the Halifax International Airport complex and is in the upper reaches of the Bennery Brook watershed. Bennery Brook is part of the Shubenacadie River system. EPS (1976) determined that acid drainage was entering the Shubenacadie River via Bennery Brook. In subsequent unpublished studies it was concluded that the present study area, which comprises less than one percent of the Bennery Brook watershed, was the source of the majority of the acid and metal loadings at

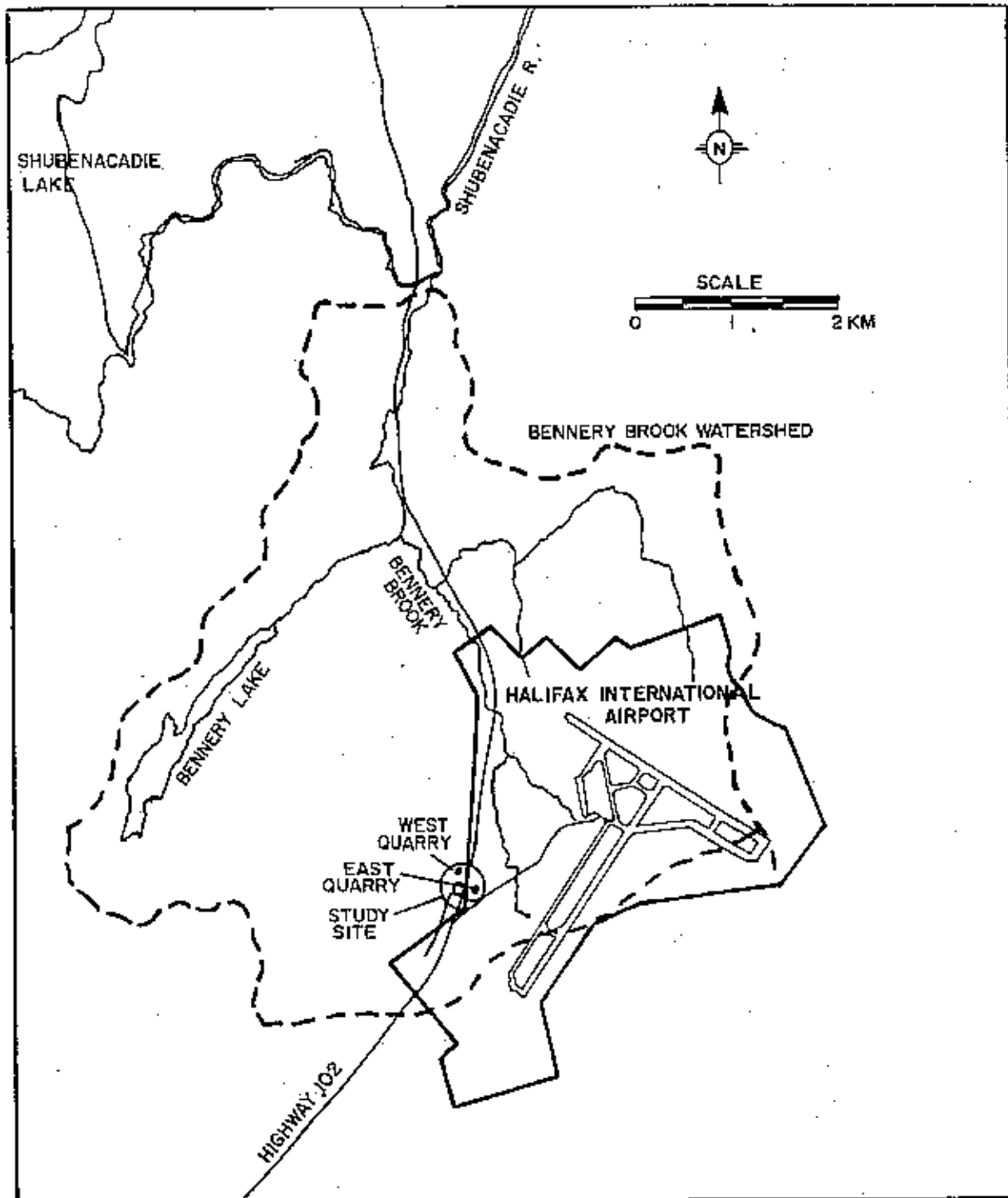


Figure 1: General Location Map

the mouth of the brook. The location of the study area is shown in Figure 1.

Surface Water Monitoring

Flow was monitored at two locations in the study area, as shown in Figure 2. Total quarry outflow was measured at a single well-defined channel at the north end of

the quarry. Surface flow from within the quarry originated from numerous small groundwater discharge areas which represent areas where bedrock was excavated to a level below the local groundwater table. A layer of iron hydroxide sludge, up to a few centimeters thick, was common in the discharge areas.

The only well-defined surface inflow to the quarry, a stream on the east side, was also monitored. During dry periods this was the only source of surface water entering the quarry. At such times it was possible to determine the quantity of groundwater discharged within the quarry by subtracting surface water inflow from

surface water outflow. Net chemical loadings from groundwater discharge were determined by the same method. That is, loadings through the inflow were subtracted from total outflow loadings.

Flow measurements were taken three times per week at the two monitoring sites. Water samples were taken at both sites

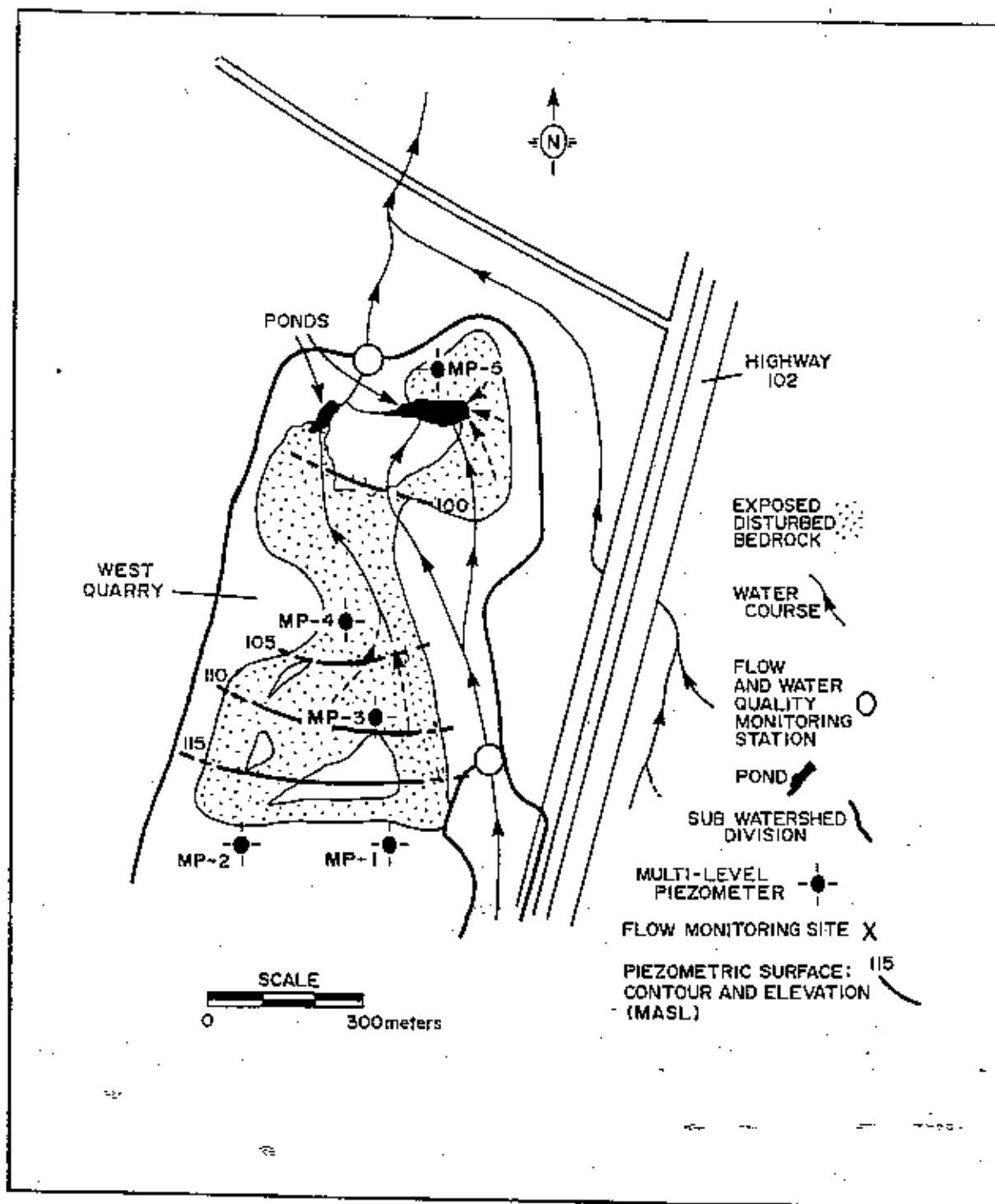


Figure 2: West Quarry Location and Drainage Map

once per week. Samples were analyzed for pH, conductivity, colour, magnesium, total organic carbon, sulphate, calcium, arsenic, copper, iron, zinc, acidity, nickel, manganese, chloride and aluminum.

Groundwater Monitoring

Five multi-level monitoring wells, MP-1 to MP-5, were installed in and around the quarry (Figure 2). They were located with the aim of observing changes in groundwater quality near and within the quarry. For the purpose of locating the wells it was assumed that the direction of shallow groundwater flow in the area followed topography. MP-1 and MP-2 were located just outside the topographically highest end of the quarry to obtain background groundwater samples. The remaining three wells were completed directly into the disturbed bedrock of the quarry to determine the effect of the disturbance on the groundwater. Piezometric surface contours on Figure 2 show that the assumed

direction of groundwater flow was generally correct.

The boreholes were 15 cm in diameter and were drilled to depths ranging from 9.5 to 12.2 m. Each contained three discrete sampling intervals except for MP-4 which, due to an error during construction, contained only two. The depth to the top of the shallowest sampling interval varied from 1.1 to 3.1 m in the five monitoring wells. Width of the intervals ranged from 3.7 to 1.9 m.

Four sets of groundwater samples were taken from each level in each well from September 12 to December 30, 1986. Groundwater was analyzed for the same parameters as surface water. In addition, *in situ* dissolved oxygen concentration was measured during the last three sampling periods. Only the data from the shallowest levels are discussed as it was assumed that they were most similar to groundwater discharge.

Table 1: Concentrations of Selected Ions in Groundwater and Quarry Drainage

		Piezometer					Quarry Drainage
		1	2	3	4	5	
Iron (meg/L mg/L)	Mean	0.004	0.005	0.565	0.636	2.133	0.309
	S.D.	0.004	0.009	0.064	0.030	0.305	0.105
Sulphate (meg/L mg/L)	Mean	0.164	0.095	1.068	0.648	7.630	3.670
	S.D.	0.045	0.016	0.090	0.060	0.924	0.454
Hardness (meg/L mg/L)	Mean	0.137	0.129	0.728	0.508	10.073	1.540
	S.D.	0.060	0.035	0.026	0.026	1.662	0.191
Alluminum (meg/L mg/L)	Mean	0.019	0.078	0.029	0.009	0.128	1.071
	S.D.	0.004	0.115	0.024	0.005	0.067	0.212
Hydrogen ion (meg/L mg/L)	Mean	0.005	0.003	0.021	0.001	0.263	0.464
	S.D.	0.002	0.000	0.022	0.000	0.453	0.168
Chloride (meg/L mg/L)	Mean	0.134	0.106	0.134	0.123	6.817	1.800
	S.D.	0.042	0.042	0.054	0.045	1.156	0.411

Results

Mean and standard deviation estimates for water quality of groundwater discharge as it reached the quarry outflow (calculated as outlined above) were determined using six sets of dry-weather samples. Estimates were also obtained for the shallowest levels of the five monitoring wells. Table 1 presents the results for selected water quality parameters.

Iron, sulphate and hardness concentrations increased from the background wells to the wells located in the quarry, with a marked increase in MP-5. Aluminum and hydrogen ions are the only parameters that are more concentrated in groundwater discharge at the quarry outflow than at MP-5. Chloride concentration is similar in MP-1 through 4, increases sharply in MP-5 and is intermediate at the quarry outflow.

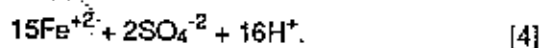
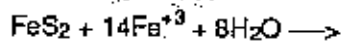
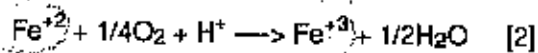
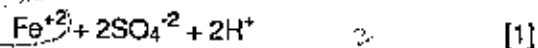
Standard deviations generally indicate that there was very little variation in water quality in the wells and in groundwater discharge as estimated at the quarry outflow. Notable exceptions are shown in iron concentrations in MP-1 and MP-2 and hydrogen ion concentrations in MP-3 and MP-5.

Average water quality of the 12 water samples from the shallowest levels of the three quarry monitoring wells was used as an estimate of the chemistry of groundwater as it discharges within the quarry. It was compared with the average water quality at the quarry outflow to test for significant changes in water quality subsequent to groundwater discharge. In addition, water quality was compared between each monitoring well and between selected groups of monitoring wells.

Comparisons were done using a one-tailed t-test (Sokal and Rohlf, 1969) which provides a measure of the probability that the difference between two means is significant. The one-tailed aspect incorporates into the test the probability that the direction of the difference between two means is indicative of the actual direction. For all tests a significance level of 0.05, or less, was used as the criterion for rejecting the null hypothesis that the two means are equal.

Discussion

The basic steps in acid generation from pyrite (FeS_2) are as follows (Stumm and Morgan, 1970):



In Equation 1 the sulphide portion of the mineral is oxidized to sulphate while dissolved ferrous iron and acidity are released. Soluble ferrous iron is oxidized to ferric iron (Equation 2) and subsequently hydrolyzed to insoluble ferric hydroxide (Equation 3). More acidity is released as ferric hydroxide precipitates out of solution.

Pyrite may also be oxidized by ferric iron as shown in Equation 4. Nordstrom (1982) stated that in the early stages of acid generation pyrite is oxidized by oxygen. As pH drops below 3.0 ferric iron becomes soluble and is the primary oxidant. Singer and Stumm (1970) concluded that the regeneration of ferric iron, through oxidation of ferrous iron (Equation 2), is the rate determining step in advanced acid drainage production. It should be noted that pyrite oxidation (Equation 1) takes place at a lower oxidation potential than that at which ferrous iron is oxidized (Equation 2).

As groundwater moves from depth and is discharged at the surface of the quarry it undergoes quality changes reflecting changing oxidizing conditions. At some point pyrite becomes unstable and the reaction in Equation 1 begins to occur. There is a significant accumulation of iron in quarry groundwater (mean of background wells 0.0045 meq/L, mean quarry wells 1.111 meq/L) indicating that there is not enough oxygen present, even near the surface, to oxidize ferrous iron (Equation

2). Therefore, only the first step of acid generation occurs below the groundwater table while the subsequent, more rapid steps, are inhibited by lack of oxygen.

The significant increase in hardness from the background to the wells (means 0.133 meq/L and 3.770 meq/L, respectively) compares closely with that of sulphate (means 0.130 meq/L and 3.115 meq/L, respectively). However, H^+ concentration does not show significant increase even though it is produced at the same rate as sulphate in the early stages of acid generation. This indicates that the dissolution of basic calcium and magnesium salts from bedrock is sufficient, at this stage, to buffer all acid inputs.

Subsequent to groundwater discharge, oxygen is no longer limiting. Concentration of H^+ increases significantly from the point where groundwater is discharged (mean of quarry wells 0.095 meq/L) and where it exits the quarry (mean 0.464 meq/L). Part of the increase is immediate and probably due to rapid conversion of iron from the ferrous to the ferric form (Equation 2) and subsequent precipitation (Equation 3). This is indicated by the thick iron hydroxide deposits at the discharge sites and by the decrease in iron concentration from groundwater to the quarry outflow (quarry outflow mean 0.309 meq/L).

Stumm and Morgan (1970) stated that as pH decreases, ferric iron no longer precipitates and the more rapid step in the acid generation process can take place (Equation 4). Therefore, assuming that pyrite is available on the surface, elevated iron concentrations in groundwater discharge will shorten the distance between the discharge point and the point at which the maximum rate of acid generation is attained on the surface of the quarry.

From the above it is apparent that the pathway through which groundwater affected by quarrying moves has an important effect on the rate of acid generation. Groundwater flowing beneath a quarry may become enriched in iron as it flows through fresh bedrock fractures. However, the amount of acidity generated by the quarry activity will be lessened if the iron-

enriched groundwater does not discharge to the quarry surface. By restricting the depth of quarry excavation the creation of discharge areas for iron-rich groundwater would be avoided.

Restricting excavation depth will not inconvenience quarry operators as it would first seem. Many of these quarries are only worked for a short time and do not have adequate drainage systems. As such, many are operated on a "to groundwater" basis because of drainage problems that arise once the groundwater table is encountered. Installation and monitoring of one or more monitoring wells at the site could provide information on groundwater level. With this information the operator could ensure that a meter or two of bedrock could be left intact between the bottom of the excavation and the top of the groundwater table.

Aluminum concentration is not significantly different between the background and quarry wells (group mean 0.053 meq/L) indicating that aluminum is not an important buffer in quarry groundwater. After discharge, aluminum concentration increases significantly (mean quarry drainage 1.071 meq/L) as aluminum dissolution from bedrock becomes an important buffer of acid generated on the surface. This suggests that groundwater supplies in the vicinity of slate quarries may be more resistant to degradation by elevated aluminum concentrations than surface water supplies.

The observed trends in aluminum also have implications with respect to monitoring for the effects of quarry development on groundwater and for collecting background groundwater information prior to quarry development. Aluminum concentrations, and also pH, may compare closely to background values even though groundwater quality has been significantly impacted from quarrying. According to the data from the quarry used in this study concentrations of iron, sulphate and hardness are more effective indicators for evaluating groundwater quality impairment by quarrying.

Significantly elevated concentrations

of chloride at MP-5 with respect to the other four monitoring wells (means 6.817 and 0.124 meq/L, respectively) indicate a hydraulic connection with the adjacent highway where salt is used for highway de-icing. In another part of this study (King, 1987) it was determined that this part of the highway was a source of highly acidified drainage because of the slate used in its construction. It is therefore probable that significantly higher concentrations of iron and sulphate at MP-5 with respect to the other two quarry wells also originate in the vicinity of the highway. Mean iron, sulphate and hardness concentrations from MP-5 were 2.133 meq/L, 7.630 meq/L and 10.073, respectively while the means for samples from MP-3 and 4 were 0.601 meq/L, 0.858 meq/L and 0.618 meq/L, respectively. As such, it is suggested that water quality data from MP-3 and 4 are more representative of groundwater affected by quarrying of Halifax Formation bedrock.

Conclusions

The presence of groundwater discharge areas within the quarry increases the rate of acid generation on the surface. Ferrous iron accumulates in quarry groundwater and after discharge is rapidly converted to ferric iron and precipitated. With the resulting drop in pH, ferric iron becomes soluble and the rate of acid generation is accelerated. Therefore, acid drainage from a new quarry may be minimized by restricting quarry excavation to a depth above the local groundwater table.

Aluminum concentration and pH of groundwater may not be appropriate for use in evaluating the impact of quarrying on groundwater. Iron, sulphate and hardness concentrations are more likely to change significantly as groundwater is affected by quarrying.

Due to contamination of MP-5 by drainage from the highway, water quality data from the other two quarry monitoring wells are more suitable for comparison with groundwater from other quarries in the Halifax Formation. Water quality in these two monitoring wells are characterized by

a higher pH, higher iron concentration and lower aluminum, sulphate and hardness concentrations than surface water leaving the quarry outflow.

Acknowledgements

The authors wish to thank John Machell and Roger Albright, both of the Environmental Protection Service, for many helpful discussions during this study. We are grateful to Terry Hennigar, John Gibb and Frank Cruikshanks of the Water Planning and Management Branch of Environment Canada for assistance related to groundwater monitoring.

Funding for this study was provided through contract No. KE201-6-0103 from the Department of Supply and Services and grant No. A4797 from the Natural Sciences and Engineering Research Council.

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