Hydrogeochemistry of the Mid-levels Area, Hong Kong

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Abstract: Groundwater and seepage samples were collected from both the natural and building-modified slopes in the highly urbanized spaces of the Mid-Levels area, Hong Kong. Groundwater in the natural slopes, although retaining some signatures from rainwater, is enriched in major cations such as Na^+, K^+, Ca^{2+} and Mg^{2+} and some anions such as HCO_3^- and SO_4^{2-}. Clearly, water-rock interactions, such as weathering of plagioclase feldspar, play a significant role in the hydrogeochemistry of this area. On the developed slopes, the subsurface hydrogeochemical system is more complex. Here samples are dominated by Na-Cl and Na-Ca-Cl complexes and vary significantly in total dissolved solid (TDS). It is evident that groundwater from the developed area is contaminated by leakage from flushing water mains (mainly sea water) to different extents. It is believed that dissolution of concrete materials may also contribute calcium to the groundwater.
Keywords: hydrogeochemistry, urbanization, water-rock interaction

1 Introduction

In Hong Kong, studies of groundwater chemistry have been somewhat few in number due to the fact that groundwater is not a major source of water for public consumption. Previous studies have been restricted to subjects such as evaluation of organic pollution of wells in the villages [4] and identification of the source of groundwater by selected chemical tracers [3]. In the last few years, we have been carrying out a project "*Groundwater Chemical Studies in the Mid-Levels Area, Hong Kong*". Water samples from natural springs and seepages from both cut and natural slopes in the Mid-Levels area of Hong Kong Island have been collected in different seasons and analyzed, and provide valuable data for further environmental studies. This paper presents some of the preliminary results from this project and discusses the fundamental process of water-rock interaction, and the major issue of the impact of urbanization on the subsurface environment.

2 Geological and Hydrogeological Background of the Study Area

The Mid-Levels area, approximately 2 km^2 in size, is situated on the northern slope of the Victoria Peak (550 mPD), on Hong Kong Island (Fig. 1). It is one of the most highly urbanized areas in the world and can be divided into two parts with significantly different modes of development. The upper part of the area (>170 mPD) is essentially a natural slope with minimum development. On the contrary, the lower part of the area has been extensively developed with residential and office buildings. Besides being dominated by high-rise buildings, the original landscape in the lower areas has been greatly modified by continuous cutting and filling of slopes. Groundwater samples from the weep-holes and drains installed in these slopes, which would otherwise be extremely difficult and expensive to collect, provide a unique opportunity to understand the physical and chemical nature of the subsurface flow system of this intensively urbanized hill-slope.

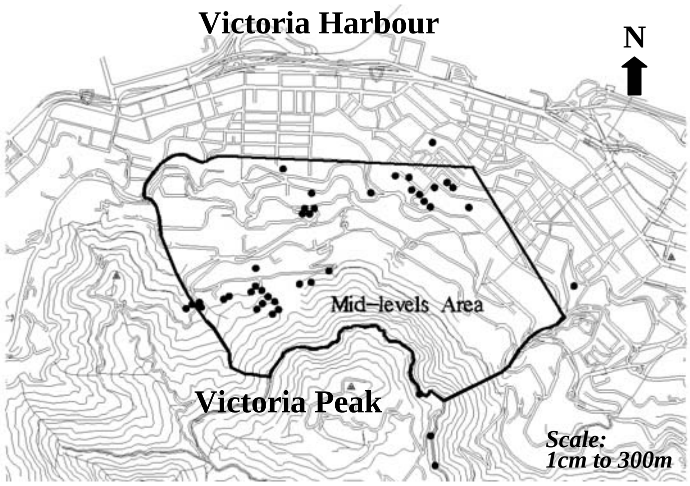

Fig. 1 Overview of the study area. Solid circles represent water sampling location

The geology and hydrogeology of the study area has been described elsewhere [3] and will be only briefly introduced here. The geology is dominated by two rock types, acidic volcanic rocks and a granitic intrusion. The volcanic rocks have been subject to low grade regional metamorphism and deformation and affected by contact metamorphism where close to the granite. Both lithologies have been subsequently intruded by basaltic dykes. The irregular contact between the granite and volcanic rocks crosses the study area and is disrupted by normal faults in several locations (Fig. 2).

In general terms, colluvium overlies several metres of decomposed rock (Grade IV to VI) above the bedrock (Grade I to III). The Hong Kong Granite underlies most of the developed area, composed of quartz (23% to 42%), potassium feldspar (31% to 42%), plagioclases (16% to 35%) and biotite (~5%). Volcanic rock underlies the upper undeveloped slopes.

Although it is thus likely that the lithologies in the subsurface are very heterogeneous and anisotropic, GCO (1982) have grouped them into three aquifer units corresponding to: a) colluvium, b) decomposed volcanic rocks and granite (Grade IV – VI), and c) volcanic and granite bedrock (Grade I – III). The colluvium contains transient and permanent perched water tables, whereas, as recently demonstrated by Jiao *et al* [7], the highly decomposed rock or saprolite (Grades IV and V) below the colluvium is relatively impermeable due to its clay-rich content. The bedrock zone along the rockhead may be fairly permeable with confined groundwater contained within a well-developed fracture network.

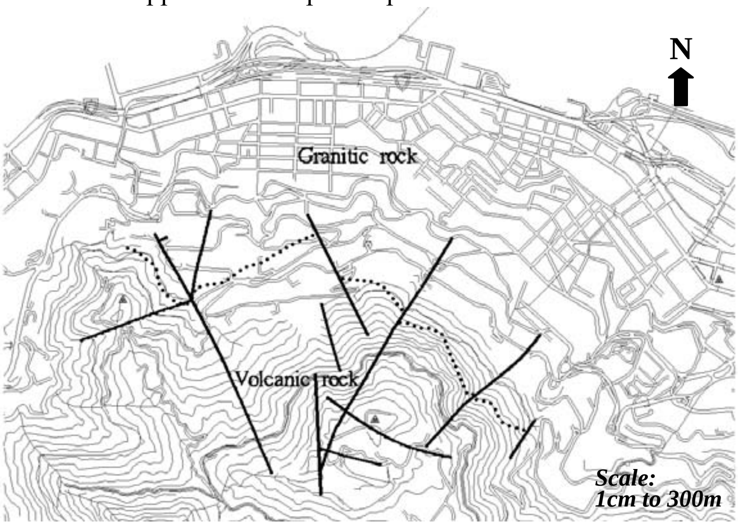

Fig. 2 Geology of the study area. Dotted lines represent the contact between granitic rock and volcanic rock. Black lines represent the locations of normal faults

3 Field and Analytical Methods

At each sampling site, the pH, temperature, electrical conductivity (EC) and dissolved oxygen (DO) of the water were measured. Samples for geochemical analyses were filtered through a hand-held Hanna filter system using a 0.45 μm cellulose filter paper, and collected in 500 ml HDPE bottles. A 125 ml sample for cation analysis was acidified to a pH of <2 using ultra-pure concentrated nitric acid. Except for Si and B which were analyzed by inductively couple plasma atomic emission spectrometer (ICP-AES), analyses for other cations were performed by inductively couple plasma mass spectrometer (ICP-MS). A second 125 ml sample was filtered and left unacidified to be used for anion analysis by HPLC Ion Chromatography. A third 125 ml sample was collected for aggressive CO_2 determination.

4 Results

4.1 Hydrogeochemical characteristics of undeveloped slopes

In Hong Kong, rainwater (the only recharge source for the natural undeveloped slopes) generally varies between pH 4 and pH 5 due to various factors such as the dissolution of NO_2 and SO_2 emitted from motor vehicles and coal-burning power stations. These pollutants may contribute some of the nitrates and sulphates to shallow groundwater. Groundwater samples collected from the natural slopes are slightly acidic (average pH = 6.08, and as low as 4.73) and have TDS less than 100 mg/L. This reflects their short residence time and low degree of water-rock interaction. They are generally free from any organic pollutant (mean [NO_3^-] is about 1.70 mg/L and no PO_4^{2-} was detected).

Although groundwater samples from the natural slopes have similar TDS, their hydrochemical facies are quite different. Six hydrochemical facies (Na-Ca-Cl-HCO_3-SO_4, Na-Ca-HCO_3-Cl, Na-Ca-HCO_3-Cl-SO_4,, Na-HCO_3-Cl, Na-Ca-Cl-HCO_3 and Ca-Na-HCO_3) were found among 18 samples. This reflects the complexity of the geology of the study area and the fact that groundwater with different flow paths may undergo different extents of water-rock interaction. Although rainwater chemistry may vary from time to time, it is generally of Na-Cl type (marine dominance) due to the regions coastal environment. It seems from the observed hydrochemical facies that the shallow groundwaters still retain a partial rainwater chemical signature (i.e. Na-Cl type), although their chemistry has been progressively modified by water-rock interaction along various flow paths. These features indicate that these groundwaters are still in their early evolutionary stage.

The nature and extent of water-rock interaction can be identified by looking at ion concentrations relative to chloride concentrations. Chloride is a useful normalizing factor because it does not enter into precipitation-dissolution processes except at brine concentrations and it rarely enters into oxidation-reduction or adsorption reactions [1]. This conservative nature makes it useful in comparison with the relative loss or gain of other ions the evaluation of which can constrain possible water-rock interactions.

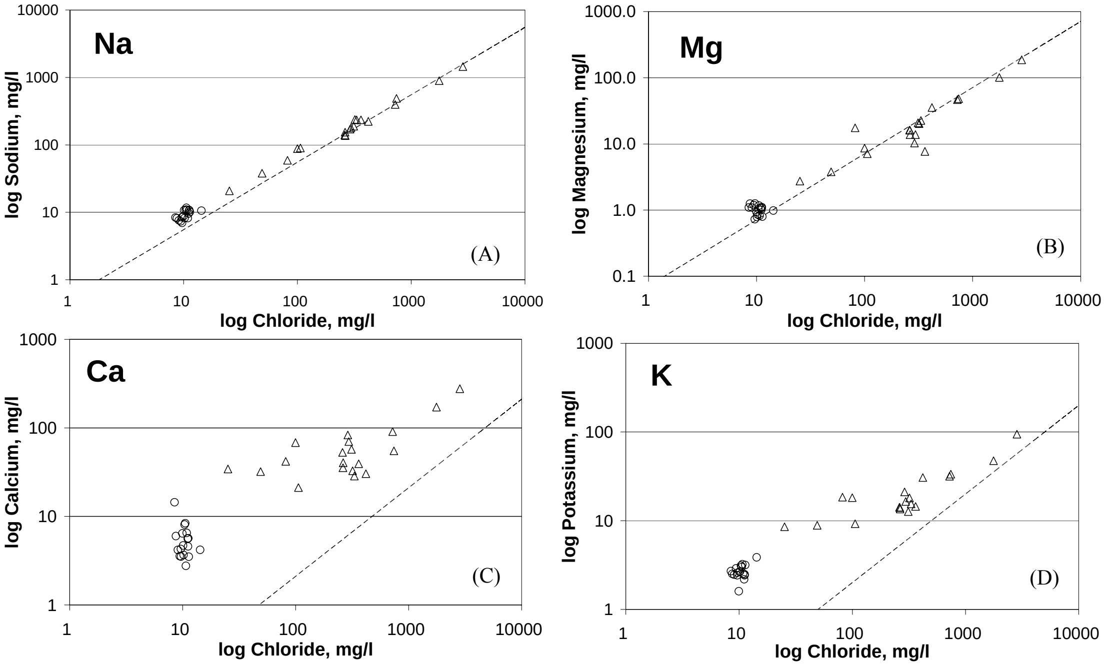

Fig. 3 Na, Mg, Ca, K concentrations plotted against Cl concentration in the Mid-Levels area. Open triangles and open circles represent samples from developed and undeveloped slopes respectively. The dotted lines represent the seawater dilution line for the corresponding cation

According to Fig. 3, all groundwater samples from the undeveloped slopes are enriched in major cations compared to the seawater. It is calculated that about 38% of Na, 26% of Mg, 92% of K and 95% of Ca in the groundwater are derived from non-marine sources. One of the major “non-marine” sources is likely to be weathering of minerals like plagioclase feldspars, K-feldspar and biotite, according to equations 1-4:

$$2NaAlSi_3O_8 + 2CO_2 + 3H_2O \rightarrow Al_2Si_2O_5(OH)_4 + 2Na^+ + 4SiO_2 + 2HCO_3 \quad (1)$$
(albite) (kaolinite)

$$CaAl_2Si_2O_8 + 2CO_2 + 3H_2O \rightarrow Al_2Si_2O_5(OH)_4 + Ca^{2+} + 2HCO_3^- \quad (2)$$
(anorthite) (kaolinite)

$$2KMg_3AlSi_3O_{10}(OH)_2 + 14CO_2 + 7H_2O \rightarrow Al_2Si_2O_5(OH)_4 + 2K^+ + 6Mg^{2+} + 4SiO_2 + 14HCO_3^- \quad (3)$$
(biotite) (kaolinite)

$$2KAlSi_3O_8 + 2CO_2 + 3H_2O \rightarrow Al_2Si_2O_5(OH)_4 + K^+ + 4SiO_2 + 2HCO_3^- \quad (4)$$
(microcline) (kaolinite)

The excess “non-marine” component of each ion (Na^+, Ca^{2+}, K^+, Mg^{2+}, and SO_4^{2-}) is calculated from the observed chloride value assuming no chloride source in the study area other than precipitation characterized by seawater values. In order to further define possible sources for the ions, statistical techniques were applied to see whether there is any correlation among Na^+, Ca^{2+}, K^+, Mg^{2+}, SO_4^{2-}, HCO_3^-, SiO_2 and NO_3^-.

Na^+ and Ca^{2+} are found to be positively correlated with HCO_3^- (R = 0.684 and R = 0.747 respectively). This implies that Na, Ca and HCO_3^- may be mainly derived from weathering of plagioclase feldspar. The generally low HCO_3^- (0.38 meq/L) indicates low degrees of water-rock interaction in the form of weathering. Na^+ and SiO_2 are linearly correlated (R = 0.760) which further confirms the source of Na and SiO_2 is likely to be from sodic feldspars (e.q. 1). At the same time, HCO_3^- (and some Ca) may be reduced by calcite precipitation since calcium deposits in the form of “tufa”, are discovered on many of the weep-holes of retaining walls in this area.

$$Ca^{2+} + 2HCO_3^- \rightarrow CaCO_3\downarrow + H_2O + CO_2 \quad (5)$$

It is suggested that plagioclase feldspar usually is the first primary mineral to weather significantly, followed by K-feldspar and biotite at later stage while quartz should be the most stable of all the minerals [5]. In fact, K-feldspars usually appear as large crystals in the groundmass in the study area. Their lower surface/volume may decrease the weathering rate. Given the short residence time of the shallow groundwater, it seems that K-feldspar and biotite may not be significantly weathered. This is reflected by the poor correlation between Mg^{2+}, K^+ and SiO_2. Other sources may also contribute Mg^{2+} and K^+ to groundwater in this case. It is clear that Mg^{2+} is positively correlated with SO_4^{2-} ($R = 0.798$) but since neither can be correlated with NO_3^-, it seems that they are not likely from an anthropogenic source such as fertilizer, but may be derived naturally from the lithologies source or from soil. In fact, the low nitrate level confirms that fertilizers are not a likely source. Another possible explanation of the SO_4^{2-} excess in shallow groundwater might be the acid rainfall. K^+ is positively correlated with NO_3^- ($R = 0.538$), and although no fertilizer is used in this area, potassium nitrate, KNO_3 appears to form in this hot and humid climate by bacterial action during the decomposition of organic material.

4.2 Hydrogeochemcial characteristics of the developed area

19 seepage samples collected in the built-up area have TDS ranging from about 250 mg/L to 5300 mg/L. They are dominated by 2 hydrochemical facies: Na-Cl and Na-Ca-Cl. Their nitrate concentrations range from 8.07 mg/L to 36.6 mg/L with average of 19.17 mg/L, which is about 11 times higher than that of the natural slopes. 6 sites (where samples have $[NO_3^-] > 25$ mg/L) are suspected to have been modified by sewage pollution. Because of the sudden elevation in TDS and nitrate levels observed in the developed area, it seems that these waters are not completely natural in origin but possibly mixed with other waters.

It is generally believed that, throughout Hong Kong, about 25% of underground service pipes are leaking to some extent. Therefore, it is reasonable to assume that seepage samples collected in the built-up area may be contaminated by leakage from such pipes. Three types of service pipes have been installed in this area: sewage water pipes, flushing water pipes, and drinking water pipes. Water carried in each of them has a unique chemical signature which is helpful for identification of leakage. From the chemical results (NO_3^-, PO_4^{2-} and NH_4^+), leakage from sewage pipes is generally insignificant on the developed slopes. Seawater has been used for flushing purpose in Hong Kong since the 1960s. Seepage samples in the built up area are generally characterized by high TDS and dominated by Na^+ and Cl^- ions, suggesting that they are contaminated by salt water. The chloride level of the seepage samples ranges from 25 mg/L to 2840 mg/L, which represents a concentration of 0.13% to 15% of seawater in which Cl^- is about 19000 mg/L. Their mean chloride level is about 500 mg/L (2.63% of seawater). Thus, except at certain sites with abnormally high TDS levels, the leakage from flushing water pipes is generally negligible. However, it should be noted that since the difference in salinity between natural groundwater (TDS = ~100 mg/L) and flushing water (TDS = ~34,500 mg/L) is great, a small leakage of flushing water could effectively "mask" the original groundwater chemistry. Drinking water has 0.5-0.6 mg/L of fluoride and TDS about 120 mg/L. Leakage from drinking water pipes is also difficult to identify because it might likewise be masked by small quantities of seawater. However, the results from the hydrochemical study suggest that there is no significant leakage from drinking water pipes in the study area.

Fig. 4 presents a semi-log plot for sodium and chloride concentration in the Mid-Levels area. There are two distinct slopes on the plot, a steep slope at low concentrations and a gentle slope at higher concentrations. The weight Na/Cl for the steep slope is approximately unity; greater than the seawater ratio of 0.55. High ratios are very typical of fresh groundwater, whilst low ratios tend to occur when another cation, usually Ca, becomes comparable to or greater than Na in concentration. The bimodal slope on this plot may imply a transition from fresh water to water possessing a saline component [6]. This reflects the change in the hydrogeochemical system in the natural slope and developed area.

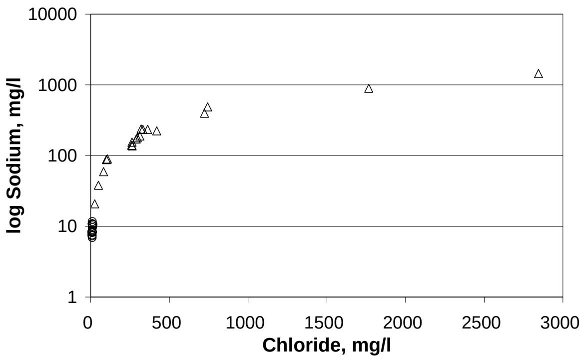

Fig. 4 Semi-log plot for sodium and chloride concentration in the Mid-Levels area. Open triangles and open circles represent samples from developed and natural areas respectively

As indicated by different cation concentrations relative to Cl^-, water-rock interaction and ion exchange processes also seem to be taking place on the developed slopes. The average Na/Cl of seepage on these slopes is 1.00 which is higher than seawater (0.85), but lower than that found on the undeveloped natural slopes. This suggests that plagioclase feldspar weathering is taking place, but to a much lesser extent. Some localities have molar Na/Cl and Mg/Cl lower than that of seawater, confirming that ion exchange is also taking place. All seepage samples from the developed slopes are enriched in Ca to the same extent as those from the natural slope. However, as indicated by the lower average Na/Cl, the concentration of cations derived from plagioclase feldspar weathering is less in the built up area. It seems reasonable to suspect another source for the observed amount of Ca.

The high-rise buildings in Mid-Levels have basements and deep foundations (some may reach 5 meters below the bedrock) constructed from concrete and permanently or periodically beneath the water table. Concrete slowly degenerates when water-soaked by leaching of cement-paste compounds. Calcium hydroxide, which constitutes some 25% of cement paste, is found in zones on aggregate surfaces and may be precipitated in voids and cracks. It is readily soluble in water to about 1200 mg/L [2].

Three widely-used indices have been employed to assess the potential aggressiveness of water towards concrete. They are the Aggressiveness Index (AI), the Langelier Saturation Index (LSI) and the Ryznar Stability Index (RSI). From Table 1, it is clear that groundwater from the natural undeveloped area can be considered highly aggressive while waters collected from seepages in the built-up area are less aggressive. Highly aggressive groundwater from the natural area would eventually flow to the built up area, and concrete in foundations and other underground structures may unavoidably be attacked, releasing Ca^{2+}.

Table 1 Comparison of different indices for concrete corrosion by water samples from natural and built up areas

Index	Natural area (n=18)			Urbanized area (n=19)			Common value of "aggressive" water
	Min.	Mean	Max.	Min.	Mean	Max.	
AI	6.26	8.04	9.42	8.79	10.35	11.38	<10
LSI	-5.27	-3.47	-2.06	-2.78	-1.20	-0.17	<-0.5 or >+0.5
RSI	10.83	13.02	15.26	7.66	9.15	11.20	>8

In summary, it seems that the hydrogeochemistry of the developed slopes area is more complex. Water rock-interaction, leakage from services and dissolution of concrete are considered to be the most important factors controlling the observed seepage chemistry.

5 Conclusions

This paper presents some of the preliminary results of a groundwater chemical study in the Mid-Levels area, Hong Kong. Groundwater chemistry in the natural slopes seems to be controlled mainly by water-rock interactions such as plagioclase weathering. Weathering of k-feldspar and biotite may take place to a lesser degree due to the short residence time of the shallow groundwater. Decomposition of organic plant material is also believed to occur in the natural slope. As they flow to the developed areas, these waters are very aggressive in attacking concrete, as demonstrated by several widely used indices. In the developed area, seepage samples have been contaminated to various extents by leakage from services, mainly salt water used for flushing. Water-rock interactions, such as weathering of plagioclase feldspar, also occur in the developed area but their effects on the chemistry of the seepage here appears less. On the other hand, as indicated by cations such as Na^+ and Mg^{2+}, ion exchange also changes the water chemistry. It seems that part of the observed calcium is released by dissolution of concrete from foundations and underground structures in the built up slopes, and the hydrogeochemical environment here is clearly far more complicated than on the natural slopes.

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