Implications of river chemistry variations on an orogenic, subtropical island - a preliminary study

The study collected water samples from three rivers in southern Taiwan to understand the temporal and spatial variations of major dissolved ions, including Na⁺, K⁺, Mg²⁺, Ca²⁺, Cl⁻, SO₄²⁻, HCO₃⁻ and H₂SiO₄, and to explore the relationships between chemical and physical weathering in an orogenic and tropical area. During 2006-2007, total dissolved solid discharge (TDS discharge) from the investigated rivers was calculated to be around 3.27 Mt/yr, and 60 % of dissolved ions were attributable to the outcrop of silicate. However, TDS discharge occupied just 3 % of total delivered material in the river water. Accordingly, physical transport plays a decisive role in weathering process with only a small fraction capable of going through chemical dissolution in reaching the river. The investigation results also show that the huge amount of water discharge in rainy seasons dilute ion concentrations, and that sea spray delivered by monsoon and compositions or properties of source rocks also induce spatial variations of dissolved ions. Additionally, areas with low strength rock have more dissolved material in the river water.

Introduction

Transportation of material in river water is an important index of weathering processes in upstream areas and also a source of deposits in ocean water (Hovius et al., 2000, Fuller et al., 2003, Dadson et al., 2004). Soils or source rocks which are subjected to weathering and erosion processes are major sources of dissolved material in river water (Smolders et al., 2004). Total dissolved solid (TDS), the total weight of dissolved material in river water, including Na⁺, K⁺, Mg²⁺, Ca²⁺, Cl⁻, SO₄²⁻, HCO₃⁻ and H₂SiO₄, is thought to reflect chemical weathering in the catchment (Gordeev and Sidorov, 1993, Qin et al., 2006). Stallard and Edmond (1983) and Berner and Berner (1987) found that lithologies dominate the chemical weathering of catchments. Pinet and Souriau (1988) pointed out that the influence of precipitation on chemical weathering is greater than that of temperature. Geological conditions dominate the spatial variation of river chemistry, and the fluctuations of water discharge affect the temporal variation (Wu et al., 2007). However, a comprehensive survey of the effects of environmental conditions on chemical weathering in an area with complex climatic and geological variations is still needed.

The active orogeny with abundant precipitation, 2600 mm per year on average, on Taiwan leads to intense erosion processes and huge amounts of deposit are delivered to river channels (CWB 1980-2008, Lin et al., 2008, Chuang et al., 2009, Chen et al., 2011). Li (1976) reported a physical denudation rate of 1300 mg/cm²/yr and a chemical denudation rate of 65 mg/cm²/yr for Taiwan. The average denudation rate is equivalent to 4 mm/yr. Taiwan’s rivers have abundant transport material, significant seasonal variation and complex geology, which make them highly suitable for exploring the key relationships between chemical weathering and environmental conditions. The study collected water samples from 3 major rivers in southern Taiwan during 2006-2007. Two rivers, the Kaoping River and Linpien River, are situated in the southwest, and one river, the Peinan River, is situated in the southeast. These investigated catchments cover three major geological divisions in Taiwan (Fig. 1a). Sedimentary formations distributed along the western foothills have major lithologies of sandstone, clay, and mudstone (Ho 1994). The low-grade metamorphic formations along the western flank of the central mountain belt have major lithologies of meta-sandstone, slate, and phyllite. And, the high-grade metamorphic formations along the eastern flank of the central mountain belt have major lithologies of schist, marble, and gneiss. The rock strengths of source rocks distributed in each river catchment were also measured in this study. By analyzing chemical compositions and investigating rock properties, the study clarified the spatial and temporal variations of river chemistry and the influences of environmental conditions on chemical weathering.

Study methods

Six sites in three river catchments were selected for sampling river water twice per month during 2006-2007 (Fig. 1b). Three downstream sites were located at the boundaries between mountain areas and plains to reduce the effect of human activities. Besides, three sites were located at upstream tributaries of the Kaoping River and Peinan River. Therefore, the study can report the variations of chemical compositions in three major rivers, Kaoping River, Linpien River and Peinan River, and three small tributaries, Laonung River, Sinwulu River and Luye River.

The sampled water was treated immediately with 0.2 μm PC filter
The values adjacent to black rectangles show the total dissolved solid concentration (mg/l). The black dashed line is the contour line of 300 mg/l total dissolved solid concentration.

Figure 1. (a) Three geological divisions are defined by the change of lithologies. Region I consists of sedimentary formations, region II consists of meta-sandstones, slates, and phyllites, and region III consists of schists, marbles, and gneiss. (b) Map of study area and sampling locations. The arrows show the total dissolved solid discharge (Mt/yr) for each river. The black rectangles indicate the sampling locations. LN, LL, HP, WL, YP, TT stand for the abbreviations of Lao-Nung station, Li-Lin station, Hsin-Pei station, Wu-Lu station, Yen-Ping station, and Tai-Tung station respectively. The values adjacent to black rectangles show the total dissolved solid concentrations (mg/l). The black dashed line is the contour line of 300 mg/l total dissolved solid concentration.

paper to separate sediment from water. The filtered water was examined to determine the concentration of dissolved ions. The analysis of dissolved ion concentrations in river water included sodium (Na⁺), potassium (K⁺), magnesium (Mg²⁺), calcium (Ca²⁺), chloride (Cl⁻) and sulfate (SO₄²⁻), alkalinity (HCO₃⁻) and silica (H₂SiO₄⁻). Cations were detected by atomic absorption spectrometer with the standard samples of each cation having an accuracy of 94-104 %. In addition, anions were detected by conductivity detector based on the theory of ion-exchange chromatography (O’Dell et al., 1984) with a limit of calibration curve ranging from 10 ppm to 40 ppm.

In this study, alkalinity (HCO₃⁻) was determined by the Gran titration method. Water samples were titrated with hydrochloric acid to a pH of 4.5. Once the pH indicator changed color to show that the hydrochloric acid had neutralized, the consumption volume of hydrochloric acid was calculated to obtain the alkalinity of the water sample. Dissolved silica (H₂SiO₄⁻) was determined by the molybdic acid deoxidization method. 0.2 ml Molybdic acid was added into 5 ml water sample to form heteropoly acid. Then, 0.2 ml oxalic acid was added in the treated water sample to resist the self-reduction reaction of Molybdic acid. A spectrophotometer was applied to determine the dissolved silica concentration under wavelengths of 400 nm.

Some studies point out that the strength of rock mass is an important factor influencing erosion processes in catchments (Lin et al., 2008, Chen et al., 2011). Therefore, an N Type Schmidt hammer was used in these 11 catchments to measure the rebound of a spring-loaded mass impacted against the surface of rock outcrops. Referring to the ISRM (1981) conversion chart, we applied the rebound value to obtain uniaxial compressive strength of rockmass in each formation. In this study the representative rock strength of a given catchment was calculated by weighting uniaxial compressive strength (UCS) with the ratios of outcrop area for each formation in the catchment.

Analysis of results

Cations

The average concentration of sodium ions in the rivers of southern Taiwan was over 10 mg/l (Table 1). In the Kaoping River, Na⁺ concentration was higher than in the other two rivers, and increased from upstream to downstream. However, Na⁺ concentration in the Peinan River decreased from upstream to downstream. The river water in the southwest had higher Na⁺ concentrations than in the southeast which appears to be due to the abundant sea spray supplied by southwest monsoon to downstream of Kaoping and Linpien rivers.

The concentration of potassium ions ranged between 1.9 mg/l and 4.4 mg/l. In the downstream of Kaoping River, K⁺ concentrations were over 4 mg/l and increased from upstream to downstream. The outcrop of sedimentary rock supplying abundant K-feldspar in the downstream area of Kaoping River apparently was the key factor. On average, K⁺ concentrations in the southwest were higher than that in the southeast.

As for magnesium ions, the downstream of the southwest rivers had Mg²⁺ concentration of over 14 mg/l. The highest Mg²⁺ concentration, exceeding 15 mg/l, was measured in the upstream tributary of Peinan River, the Luye River. An obvious difference of Mg²⁺ concentration between the Luye River and the Sinwulu River is attributable to the change of lithologies. Because Phyllites and slates made up of mainly fine-grained mica are both prevalent minerals outcropping in the Luye River catchment, Mg²⁺ concentration in the Luye River catchment was higher than that measured in other upstream catchments along the Peinan River.

The highest calcium ion concentration was measured in the

| River       | Na  | K   | Mg  | Ca  | Cl  | SO₄⁻ | HCO₃⁻ | SiO₂⁻ |
|-------------|-----|-----|-----|-----|-----|------|-------|-------|
| Kaoping R.  | 16.22 | 4.36 | 14.43 | 62.12 | 17.17 | 82.97 | 167.95 | 13.92 |
| *Laonung R. | 14.35 | 1.90 | 11.20 | 36.91 | 5.15  | 73.10 | 111.66 | 9.70  |
| Linpien R.  | 12.06 | 3.17 | 14.87 | 59.42 | 15.15 | 53.91 | 188.23 | 12.86 |
| Peinan R.   | 10.68 | 2.55 | 11.32 | 50.10 | 5.18  | 105.09 | 92.44  | 11.21 |
| *Sinwulu R. | 11.14 | 2.22 | 6.02  | 49.40 | 4.93  | 95.84 | 84.35  | 11.24 |
| *Luye R.    | 12.98 | 2.72 | 15.11 | 42.96 | 4.12  | 102.30 | 99.91  | 11.48 |

R: River; *tributary of the Kaoping River; †tributary of the Peinan River.
downstream of Kaoping River. Calcite in mudstone outcrop is the major factor producing abundant Ca\(^{2+}\) in the downstream of Kaoping River. The rivers in the southeast had lower Ca\(^{2+}\) concentrations. The downstream area had higher Ca\(^{2+}\) concentrations than did the upstream. The Ca\(^{2+}\) concentration in the Peinan River catchment varied slightly, implying that the source of Ca\(^{2+}\) for the whole Peinan River catchment is relatively stable.

**Anions**

The concentrations of chloride ions displayed an increasing trend from upstream to downstream (Table 1). In the downstream of Kaoping River and Linpien River, a Cl\(^{-}\) concentration of over 15 mg/l was measured. However, the Peinan River had a Cl\(^{-}\) concentration of below 6 mg/l where the sources of Cl\(^{-}\) were affected by sea spray and geomaterial compositions. Therefore, high Cl\(^{-}\) concentration in the southwest is attributable largely to the influence of precipitation induced by southwest monsoon and mudstone outcropping in the catchments.

The major sources of sulfate ions include sea spray, sulfate in the catchment areas and human pollution (Rasch et al., 2000; Sakihama et al., 2008). Concentrations in excess of 80 mg/l SO\(_4^{2-}\) were measured in the downstream of Kaoping River. The high SO\(_4^{2-}\) concentration in the Kaoping River is attributable to the outcrop of mudstone because mudstone is rich in pyrite (FeS\(_2\)), which is prone to oxidize into sulfuric acid (Fasiska et al., 1974). The Peinan River in the east had a high average SO\(_4^{2-}\) ion concentration of over 80 mg/l, which can also be attributed to the outcrop of mudstone and some gypsum outcrops.

The concentration of alkalinity was highest among the anions measured in the study. The main sources for natural alkalinity are rocks with carbonate, bicarbonate, and hydroxide compounds. The mudstones distributed in the southwest area contribute to alkalinity. Therefore, there were higher alkalinitites in excess of 150 mg/l in the Kaoping and Linpien rivers. Although the outcrop of marble in the Peinan River catchment should contribute to carbonate into water, the mudstone with a high dissolution rate induces a greater contribution than does marble. Hence, there was higher alkalinity in the southwest.

The concentration and distribution of dissolved silica was unlike that of other dissolved ions examined in this study. The variation of H\(_4\)SiO\(_4\)\(^{-}\) concentration in southern Taiwan was small. A higher H\(_4\)SiO\(_4\)\(^{-}\) concentration was measured in the downstream area of Kaoping River. Because silicate is a very common composition in rocks, abundant sources resulted in small spatial variation of dissolved silica in Taiwan.

**Total dissolved solid (TDS)**

The total dissolved solid discharge was estimated by combining each ion concentration with water discharge. During 2006-2007, the average TDS concentration of 3 rivers was 341 mg/l, more than five times the global average of 65 mg/l (Meybeck and Helmer 1989). The total TDS discharge from the 3 rivers was 3.27 Mt/yr. The Kaoping River had the highest TDS discharge of 2.29 Mt/yr and the Linpien River had the lowest TDS discharge of 0.17 Mt/yr (Table 2). If considering the influence of catchment size, the TDS discharge can be normalized by catchment area into TDS yield (tons/km\(^2\)/yr). Southwest rivers had relatively higher TDS yields than southeast ones.

### Table 2. Total dissolved solid and total suspended sediment during 2006-2007

| River       | TDS discharge (Mt/yr) | TDS yield (tons/km\(^2\)/yr) | TSS discharge (Mt/yr) | TSS yield (tons/km\(^2\)/yr) | TSS: TDS |
|-------------|-----------------------|-------------------------------|-----------------------|-------------------------------|----------|
| Kaoping R.  | 2.29                  | 791                           | 179.9                 | 62146                         | 1:99     |
| Laonung R.  | 0.56                  | 688                           | 9.45                  | 25720                         | 3:97     |
| Linpien R.  | 0.17                  | 521                           | 2.21                  | 7132                          | 7:93     |
| Peinan R.   | 0.81                  | 511                           | 64.04                 | 40422                         | 1:99     |
| Sinwulu R.  | 0.32                  | 502                           | 12.49                 | 19553                         | 3:97     |
| Luye R.     | 0.22                  | 456                           | 11.63                 | 24419                         | 2:98     |

R.: River; TDS: total dissolved solid; TSS: total suspended sediment measured by Water Resources Agency of Taiwan (WRA, 2006-2007); *tributary of the Kaoping River, †tributary of the Peinan River

Comparing TDS discharge with total suspended sediment (TSS) discharge measured by the water resources agency of Taiwan reveals that TSS discharge in most rivers occupied more than 90 % of total transported material in the river water (Table 2). In the Kaoping River, which had high TDS discharge, the TSS discharges occupied some 99% of total material in water. This implied that material produced by physical weathering was extremely greater than chemical weathering. The average contribution from chemical weathering was only 3% in the investigated catchments, and the contribution from physical weathering was 97%.

### Environmental influences on water chemistry

**Seasonal and geographical effects**

We selected five kinds of dissolved ions, including Na\(^+\), K\(^+\), Mg\(^{2+}\), Cl\(^-\) and SO\(_4^{2-}\) which had obvious spatial variations to explore the seasonal and geographical effects on river chemistry (Fig. 2). The ratio of water discharge in rainy seasons to dry seasons (Q\(_{\text{rainy}}\)/Q\(_{\text{dry}}\)) in the Kaoping, Linpien and Peinan River were 12.2, 52.5, and 7.0 respectively.

On average, the ratios of cation concentration in rainy seasons to dry seasons was 0.56 for Na\(^+\), 0.63 for K\(^+\) and 0.75 for Mg\(^{2+}\), which meant that Na\(^+\), K\(^+\) and Mg\(^{2+}\) concentrations in dry seasons were around 1.8, 1.6 and 1.3 times greater than those in rainy seasons. The ratios decrease with the increase of Q\(_{\text{rainy}}\)/Q\(_{\text{dry}}\) ratio, which means that cation concentrations are greatly influenced by variations of water discharge (Fig. 2). The effect of dilution by water is obvious, given the apparent seasonal difference of water discharge. The rivers in the southwest displayed more obvious seasonal difference of water discharge than did those in southeast; therefore, the seasonal difference of cation concentrations in the southwest was more obvious.

Abundant water discharge in rainy seasons also caused anion concentration in dry seasons to be higher than in rainy seasons. Cl\(^-\) concentrations in dry seasons were higher than in rainy seasons, especially in the southwestern rivers, the Kaoping and the Linpien rivers. Cl\(^-\)/Cl\(_{\text{dry}}\) ratio decreased with the increase of Q\(_{\text{rainy}}\)/Q\(_{\text{dry}}\), which indicated that greater difference of water discharge between rainy and dry seasons would accompany more intense dilution. It also has been noted that the Cl\(^-\) applied by air currents from ocean is also a factor to cause higher Cl\(^-\) concentration in the southwest. However, dilution of SO\(_4^{2-}\) concentration in the southwest rivers was slighter than for Cl\(^-\) concentrations. This could be attributed to the
outcrop of gypsum (CaSO$_4$·2H$_2$O) and pyrite (FeS$_2$) which supplied abundant SO$_4^{2-}$ both in the southeast and southwest.

In summary, three major effects on dissolved ion concentrations include: (1) dilution process in rainy seasons, (2) compositions of source rock, and (3) sea spray delivered by air current from the ocean. Sea spray and water discharge can be classified as external factors, and the composition of source rock should be regarded as an internal factor. The seasonal difference of ion concentration could be attributed to the variations of external factors, but the spatial difference of ion concentration should be attributed to both external and internal factors.

**Influence of rock compositions and properties**

The relationship between Ca$^{2+}$/Na$^+$ and Mg$^{2+}$/Na$^+$ reflects the contribution ratios of silicate and carbonate in each catchment. The Na-normalized ratios are shown in a log-log space, and the end member compositions of silicate, carbonate and evaporite, adopted from Gaillardet et al. (1999). Because evaporite outcrop is rare in Taiwan, the end member compositions of silicate and carbonate dominate the contribution ratios of silicate and carbonate. (b) The relationship between average rock strength and total dissolved solid in each catchment. Nevertheless, some 20 % - 40 % of dissolved ions were produced from carbonate. Notwithstanding the lesser aerial extent of the carbonate rocks, the ratio of dissolved ions from carbonates imply high dissolved factor of carbonate caused a considerable amount of dissolved ions to enter the water.

Rock of high strength can resist weathering processes; therefore, it produces little dissolved material. Comparison between the TDS discharge and average uniaxial compressive strength (UCS) of each catchment revealed that catchment with higher UCS would produce less TDS (Fig. 3b). The average UCS of catchments in the southwest is lower than that in the southeast. Therefore, high TDS discharge was measured in the southwest river. This implied that mechanical properties of the source rock would influence not only physical weathering but also chemical weathering.

**Conclusions**

The ion concentration distribution in the study area showed that ion concentrations increased from east to west, and from upstream to downstream. This can be attributed to three factors: air currents from the ocean, water discharge variation, and the composition variations of source rock. Silicate-bearing rocks are common in Taiwan and contributed 60 % of total dissolved ion. The river catchments in the downstream of the Kaoping River with lower rock strength had higher ion concentration, which implied that mechanical properties of rocks in the catchments affect not only physical weathering but also chemical weathering. Plentiful water discharge in rainy seasons resulted in the dilution of dissolved ion concentration in rainy seasons and thus lower concentration than in dry seasons. In addition, sea spray delivered by southwest monsoon supplied dissolved ions to catchments in the southwest. In summary, total dissolved solid of 3.27 Mt/yr was delivered to downstream or ocean, which occupied just 3 % of total delivered material. This implied that physical weathering still provided
most of the delivered material on an island characterized by intense weathering rates and complex climatic and geologic conditions.

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