

Chemical and physical weathering in a mountainous tributary of the Zhujiang (Pearl River), China

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Abstract The historical records of dissolved and particulate solids transported in rivers can provide important information about long-term chemical and physical denudation in the drainage basins, as well as the atmospheric CO₂ consumption. In this study, temporal variations of major ions and suspended sediment between two separate periods 1959–1967 and 1991–1999 in a mountainous tributary of the Zhujiang (Pearl River) in China were examined using statistical methods. Suspended sediment and most major ions, as well as total dissolved solids (TDS) showed significant downward step changes between these two periods. Chemical weathering rate, especially silicate weathering rate, and atmospheric CO₂ consumption rate decreased in the later period, coinciding with the decreasing of mechanical erosion rate. The positive relationship between dissolved and suspended solids suggests a strong coupling between chemical and physical weathering rate in the drainage basin.

Key words trend analysis; major ions; suspended sediment; chemical and physical weathering; the Zhujiang (Pearl River); atmospheric CO₂ consumption rate

INTRODUCTION

The relationship between physical erosion and chemical weathering of silicates has been debated based on the database of global rivers. Millot *et al.* (2002) developed a global power law between chemical erosion and physical erosion of granitoid and basaltic watersheds, which can be expressed as: $\text{Chem} = 0.39 \times (\text{Phy})^{0.66}$. Although this relationship had its limited application in the regions with high physical erosion rates, the importance of control of chemical weathering of silicates by physical erosion has been suggested in other global and regional studies (Gaillardet *et al.*, 1995, 1999; France-Lanord *et al.*, 2003). Although the relationship between physical erosion and chemical weathering of silicates has been well highlighted in the global scale, there are fewer reports about the response of chemical weathering rates to physical erosion in the single river system. Decreasing trends of total dissolved solids (TDS) and some major ions, especially the sum of Na⁺ and K⁺, were reported to coincide with sediment load decreasing in the Dongjiang, one of the main rivers of the Zhujiang (Zhang *et al.*, 2007). Gao *et al.* (2001) also reported positive relationships between HCO₃³⁻ concentration and total suspended sediment (TSS) concentration in the Xijiang and the Beijiang and suggested the enhancement of chemical weathering under intense physical weathering. The above studies imply that the control of chemical weathering by physical erosion may also be important in the single river system.

This study investigates the relationship between chemical and physical weathering in a mountainous tributary of the Zhujiang (Pearl River), where land use changes have been taking place in the catchment, and significant changes were observed in both sediment transport and solute transport.

STUDY AREA

The Luodingjiang River drains an area of 4493 km² and runs a total length of 201 km before joining into the main channel of the Lower Xijiang, which is the main tributary of the Zhujiang (Pearl River), China. In the catchment, coarse-grained granites and poorly cemented purple siltstones/sandstones are highly erodible and very susceptible to soil erosion. Historically, the Luodingjiang River basin has been ranked as a region with serious soil erosion in Guangdong province and the Luodingjiang River is termed “Little Huanghe (Yellow River)” by local people. Reforestation has been implemented in the catchment since the middle 1980s.

DATA SERIES AND METHODS

The data records on annual water discharge and sediment yield as well as major ions (Ca^{2+} , Mg^{2+} , $\text{Na}^+ + \text{K}^+$, HCO_3^- , SO_4^{2-} , Cl^-) measured in the Luodingjiang River over the period 1959–1999 were collected from the Guanliang Hydrological Station in the catchment. However, the data series of major ions were not continuous through the whole period 1959–1999. The records for most of the major ions were only available in the two separate periods 1959–1967 and 1991–1999 due to the impact of the Cultural Revolution in China. Hence, all the analysis conducted was based on the two periods: 1959–1967 and 1991–1999. For the first period (1959–1967), the sampling frequency for major ion chemistry analysis was monthly, or at higher frequency (e.g. 3 times per month), while for the second period (1991–1999), the sampling frequency was quarterly. The data series of annual water discharge and sediment yield are plotted in Fig. 1 and monthly major ions, the total dissolved solid (TDS) and pH are plotted in Fig. 2, for visualizing the data and possible existence of general trends.

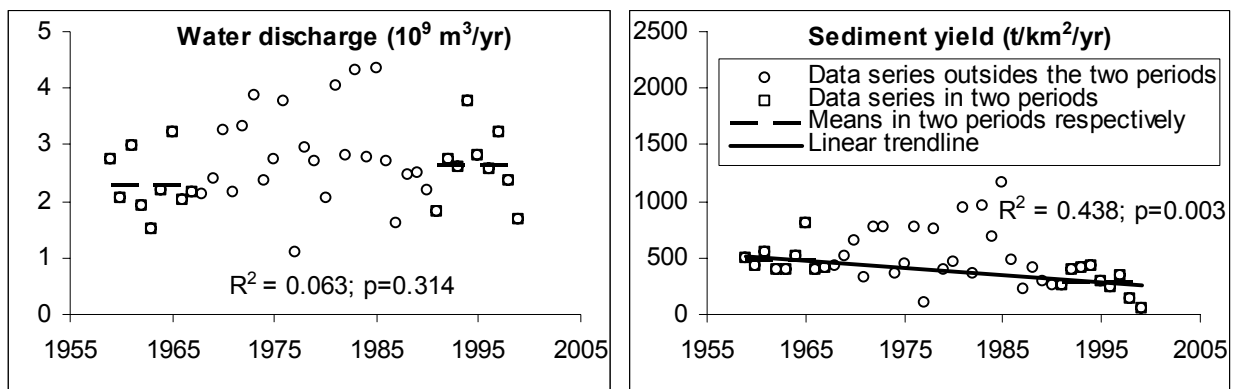


Fig. 1 Visualization of the long-term series of annual water discharge and sediment yield of the Luodingjiang River during the period 1959–1999. The linear trendline is based on the data series in the two periods. R^2 is the coefficient of determination of the linear regression model and p is the significance level.

Step change between the two separate periods was firstly investigated for all data series. Non-parametric statistical procedures were employed in order to cope with missing data, outliers, non-normal distribution, and seasonality in the data series. For water discharge and sediment yield, rank-sum test Wilcoxon (1945) and associated Hodges-Lehmann (H-L) estimator of magnitude (Hodges & Lehmann, 1963) were chosen. For major ions and the total dissolved solids, procedures with seasonality consideration were applied (see Helsel & Hirsch, 1992). Due to the different sampling frequencies in the two periods, the season in this study was defined as quarter on the basis of the lower sampling frequency during the period 1991–1999. For the data series sampled monthly or more frequently during the period 1959–1967, the value of the season was defined as the observation closed to the midpoint of the quarter.

RESULTS AND DISCUSSION

Step changes of water discharge and sediment yield between the two periods

The statistical results of rank-sum test and associated Hodges-Lehmann estimator are shown in Table 1. Water discharge showed a slight increase from the period 1959–1967 to the period 1991–1999, not significant at 0.05 level. Sediment yield showed a significant decrease between the two periods.

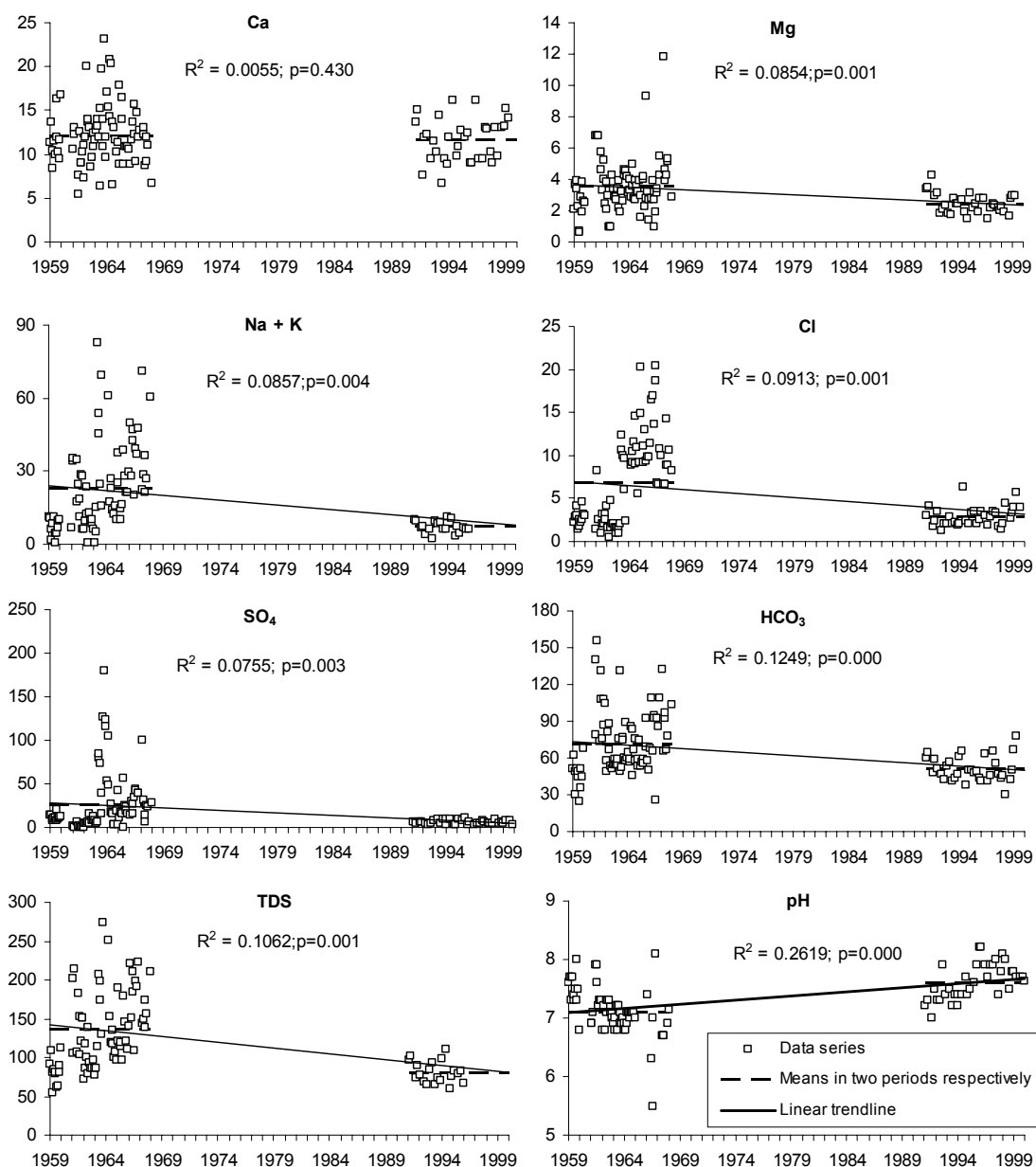


Fig. 2 Visualization of the long-term series (mg/L) of major ions and the total dissolved solids (TDS) of the Luodingjiang River during the period 1959–1999. R^2 is the coefficient of determination of the linear regression model and p is the significance level.

Table 1 Step change detection results of water discharge and sediment yield between the two periods of 1959–1967 and 1991–1999. The statistics significant at 0.05 level are marked in bold.

Parameter	Rank-sum test			Hodges-Lehmann estimator	
	W_r	Change	Δ_{HL}	Δ_{HL} lower	Δ_{HL} upper
Water discharge (10^9 m ³ /year)	75	+	-0.41	-0.90	0.35
Sediment yield (t/km ² /year)	115	-	157.63	61.53	349.79

Step changes of major ions chemistry between the two periods

The statistical results of seasonal ran-sum test and associated seasonal Hodges-Lehmann estimator are shown in Table 2. The total dissolved solids (TDS) and most of major ions except Ca^{2+} in the

period 1959–1967 were significantly different from those in the period 1991–1999 at 0.05 level. The change directions were downward and the amplitudes of shift are indicated by the associated seasonal Hodges-Lehmann estimators. pH showed a upward change but not significant at 0.05 level.

Table 2 Step change detection results of major ion chemistry between the two periods of 1959–1967 and 1991–1999. The statistics significant at 0.05 level are in bold.

Parameter	Seasonal rank–sum test				Seasonal Hodges–Lehmann estimator		
	W_{rs}	Z_{rs}	Change	p	Δ_{SHL}	Δ_{SHL} lower	Δ_{SHL} upper
Ca ²⁺	296	0.778	–	0.437	0.40	–2.20	2.84
Mg ²⁺	351	2.172	–	0.030	0.85	–0.10	1.89
Na ⁺ + K ⁺	260	2.175	–	0.030	14.18	1.65	34.70
Cl [–]	322	1.981	–	0.048	4.23	–0.42	7.68
SO ₄ ^{2–}	366	2.249	–	0.025	8.05	–0.54	21.39
HCO ₃ [–]	358	2.199	–	0.028	11.85	–1.40	37.51
TDS	263	2.868	–	0.004	48.80	7.90	119.40
pH	141	–1.729	+	0.084	–0.40	–0.90	–0.10

Changes of chemical weathering rate and atmospheric CO₂ consumption rate between the two periods

The specific chemical weathering rates (t/km²/year) for different rocks (silicates, carbonates, evaporites, and sulfides when assumed) and the specific total chemical weathering rate were calculated based on the total dissolved solids (TDS) derived from the forward model based on mass budget of cations (see Garrels & Mackenzie, 1967; Meybeck, 1987; Moon *et al.*, 2007). The calculation results are shown in Table 3. The total rock weathering rate on average was 149 t/km²/year in the first period and 79 t/km²/year in the second period when all sulfate was assumed to come from gypsum, and 114 and 67 t/km²/year in the two periods, respectively, when all sulfate was assumed to come from pyrite oxidation. In the both situations of sulfate sources, the total chemical weathering rates appeared to decrease in the second period compared to those in the first period. The chemical weathering rates of silicates, evaporites and sulfides (when assumed) showed the similar characteristics. However, the carbonate weathering rates slightly increased from the first period to the second period. Higher chemical weathering rates of total rocks, silicates, and evaporites but lower chemical weathering rates of carbonates and sulfides were observed when all sulfate was assumed to come from gypsum compared to the situation when all sulfate was assumed to come from sulfide oxidation. This indicates that neglecting the sulfide weathering could overestimate the silicate and evaporite chemical weathering rates but slightly underestimate the carbonate weathering rate.

The important issue related to the chemical weathering is the CO₂ consumption via chemical weathering, especially silicate weathering, which is a key factor for regulating the global CO₂ level and climate change. Based on the reaction equations of sequestering atmospheric CO₂ via carbonic acid attached chemical weathering (both carbonate and silicate), the total atmospheric CO₂ consumption (in mol/year) as well as the respective atmospheric CO₂ consumption via carbonate and silicate weathering can be calculated. The atmospheric CO₂ consumed by the total rock weathering, carbonate weathering, and silicate weathering can be expressed by the following equations:

$$[\text{CO}_2]_{\text{total}} = [\text{CO}_2]_{\text{cab}} + [\text{CO}_2]_{\text{sil}} \quad (1)$$

$$[\text{CO}_2]_{\text{cab}} = [\text{Ca}]_{\text{car}} + [\text{Mg}]_{\text{car}} \quad (2)$$

$$[\text{CO}_2]_{\text{sil}} = [\text{Na}]_{\text{sil}} + [\text{K}]_{\text{sil}} + 2[\text{Ca}]_{\text{sil}} + 2[\text{Mg}]_{\text{sil}} \text{ if } [\text{SO}_4]_{\text{riv}} = [\text{SO}_4]_{\text{eva}} \quad (3)$$

or

$$[\text{CO}_2]_{\text{sil}} = [\text{Na}]_{\text{sil}} + [\text{K}]_{\text{sil}} + 2[\text{Ca}]_{\text{sil}} + 2[\text{Mg}]_{\text{sil}} - 2[\text{SO}_4] \text{ if } [\text{SO}_4]_{\text{riv}} = [\text{SO}_4]_{\text{sul}} \quad (4)$$

The calculation results of the specific atmospheric CO₂ consumption rates (in 10³ mol/km²/year) are shown in Table 3. The total CO₂ consumption rate on average in the Luodingjiang River was 705 × 10³ mol/km²/year in the first period and 415 × 10³ mol/km²/year in the second period when all sulfate was assumed to come from gypsum, and 559 and 366 × 10³ mol/km²/year, respectively, when all sulfate was assumed to come from pyrite oxidation involved with silicate weathering. For both situations of sulfate sources, the total CO₂ consumption rate and the CO₂ consumption rate via silicate weathering were significantly smaller but the CO₂ consumption rate via carbonate weathering was slightly larger in the second period than in the first period. Higher atmospheric CO₂ consumption rates of total rock weathering and silicate weathering but lower atmospheric CO₂ consumption rates of carbonate weathering were observed when all sulfate was assumed to come from gypsum compared to the situation when all sulfate was assumed to come from sulfide oxidation involved silicate weathering. This indicates that neglecting the sulfide weathering would overestimate the chemical weathering rates and the atmospheric CO₂ consumption rates by silicate weathering.

Table 3 Chemical weathering rates (t/km²/year) and atmospheric CO₂ consumption rates (10³ mol/km²/year) calculated from mass balance models.

	Silicate weathering		Carbonate weathering		Evaporite weathering	Sulfide weathering	Total rock weathering	
	TDS (t/km ² /year)	CO ₂ cons. (10 ³ mol/km ² /year)	TDS (t/km ² /year)	CO ₂ cons. (10 ³ mol/km ² /year)	TDS (t/km ² /year)	TDS (t/km ² /year)	TDS (t/km ² /year)	CO ₂ cons. (10 ³ mol/km ² /year)
1959–1967								
max	349	2402	60	293	121	–	435	1898
min	12	80	–23	103	2	–	55	235
mean	90	621	30	198	29	–	149	705
1991–1999								
max	53	364	57	333	19	–	108	576
min	6	39	23	117	5	–	52	269
mean	28	189	41	225	10	–	79	415
1959–1967								
max	215	1297	65	410	27	84	291	1385
min	3	106	4	25	0	0	40	83
mean	55	329	36	230	9	14	114	559
1991–1999								
max	36	223	59	374	9	8	92	526
min	4	51	24	154	1	3	45	240
mean	16	91	43	274	3	5	67	366

Relationships of chemical weathering and physical erosion

Using all the available records of major ions and the corresponding water discharge and suspended sediment at the sampling time (monthly or more frequently in the period 1959–1967 and quarterly in the period 1991–1999), the relationships of all dissolved ions with water discharge and the total suspended sediment were investigated in the two periods, respectively. The standard rating relationship between dissolved species and water discharge can be expressed as the following double log linear equation (Walling & Webb, 1986):

$$C = aQ^b \quad (5)$$

where C is the concentration (mg/L) of major ions or TDS and Q is water discharge (m³/s). In this study, the equation is also applied to express the relationship between dissolved species and total suspended sediment as follows:

$$C = aTSS^b \quad (6)$$

where TSS is the total suspended sediment concentration (mg/L).

The results of rating relationships between solute concentrations and water discharge as well as total suspended sediment are summarized in Table 4. The characteristics of these relationships in the two periods showed great difference. In the period 1959–1967, the relationships were very complicated and different responses were observed for different ions. Ca^{2+} , Mg^{2+} , and HCO_3^- showed inverse relationships with both water discharge and total suspended sediment concentration with $b < 0$. The sum of Na^+ and K^+ , Cl^- , and SO_4^{2-} showed positive relationships with both water discharge and total suspended sediment concentration with $b > 0$. TDS showed an inverse relationship with water discharge, but a positive relationship with total suspended sediment concentration. In the period 1991–1999, b had negative values for the relationships of each dissolved component, as well as TDS with both water discharge and suspended sediment, although only significant for the relationship between TDS and water discharge at the 0.05 significance level. The negative values of b indicate inverse relationships between dissolved major ions and water discharge as well as total suspended sediment, mainly reflecting the dilution effect of water discharge or sediment on dissolved species. The negative values of b lay in the range of 0 ~ -1, mostly close to 0, which indicates that the decrease of major ion concentrations accompanying increasing water discharge is very minor. The limited dilution observed in the Luodingjiang River is similar to results from the main rivers of the Zhujiang (Zhang *et al.*, 2007), and Changjiang (Chen *et al.*, 2002), but markedly different from other rivers, where b is generally very close to -1 (e.g. the Congo (Probst *et al.*, 1992), the Humber rivers (Jarvie *et al.*, 1997) and the Seine River (Roy *et al.*, 1999).

Table 4 Double log liner relationships $C = aQ^b$ between major ion concentrations C (mg/L) and water discharge Q (m^3/s), and $C = aTSS^b$ between major ions concentrations C (mg/L) and total suspended sediment TSS (mg/L)*.

	1959–1967				1991–1999			
	Q		TSS		Q		TSS	
	b	p	b	p	b	p	b	P
Ca^{2+}	-0.112	0.000	-0.048	0.000	-0.069	0.319	-0.048	0.125
Mg^{2+}	-0.036	0.259	-0.001	0.986	-0.120	0.137	-0.043	0.250
$Na^+ + K^+$	0.046	0.419	0.130	0.007	-0.107	0.605	-0.072	0.287
Cl^-	0.285	0.000	0.287	0.000	-0.160	0.179	-0.025	0.656
SO_4^{2-}	0.029	0.741	0.187	0.012	-0.214	0.059	-0.037	0.492
HCO_3^-	-0.107	0.000	-0.041	0.028	-0.083	0.182	-0.044	0.123
TDS	-0.036	0.170	0.023	0.279	-0.176	0.036	-0.053	0.060

*values in bold indicate significant at 0.05 level.

The different responses of dissolved species to the rising water discharge and sediment transport between two periods are closely related to the different characteristics of physical erosion in these two periods. As discussed in an earlier section, the sediment yield in the Luodingjiang River has experienced a dramatic decrease since the middle 1980s, while the water discharge did not show a significant change. The mean sediment yield in the first period was about twice that in the second period and the maximum sediment yield was 18 times that of the minimum sediment yield during these two periods (Fig. 1). The impacts of sediment transport on the dissolved species can be further illustrated by investigating the relationships between dissolved ions and sediment concentration in different sediment concentration ranges in the first period. Figure 3 plots the relationships between TDS and TSS in two sediment concentration ranges: $TSS < 300$ mg/L (Fig. 3(a)) and $TSS \geq 300$ mg/L (Fig. 3(b)). When TSS was less than 300 mg/L, TDS concentration slightly decreased with increasing suspended sediment concentration, which reflected the dilution effect, although the relationship was not significant. When TSS was above

300 mg/L, TDS concentration increased with increasing suspended sediment concentration (at 0.10 level), which reflected the flushing effect. The highly positive relationship between TDS flux and suspended sediment flux in Fig. 4 further corroborates the flushing effect of sediment on the dissolved load and suggest the strong coupling between chemical and physical weathering.

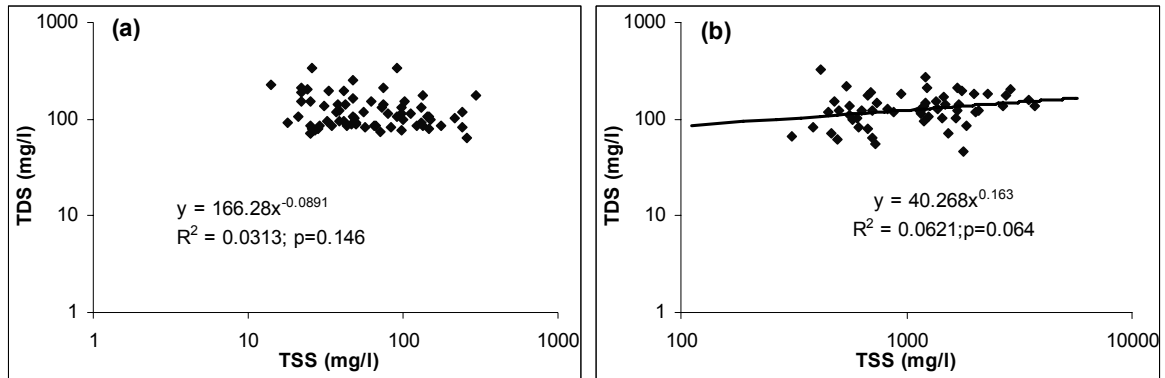


Fig. 3 Relationships between TDS concentration and TSS concentration in the period of 1959–1967 (a) when TSS < 300 mg/L; (b) when TSS ≥ 300 mg/L.

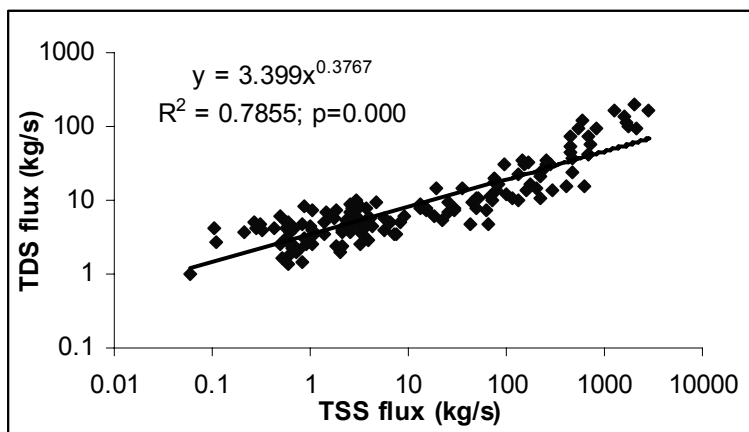


Fig. 4 Relationship between TDS flux and TSS flux in the Luodingjiang River.

CONCLUSIONS

Both sediment load and major ion chemistry have changed significantly between the two separate periods: 1959–1967 and 1991–1999. The sediment yield, total dissolved solids and most of the major ions, except Ca^{2+} , showed significant downward changes during these two periods. pH showed significant upward changes during these two periods. The sum of Na^+ and K^+ , Cl^- , and SO_4^{2-} showed positive relationships with both water discharge and total suspended sediment in the first period, which reflected a purging effect or flushing effect rather than the dilution effect of water discharge which occurred in most river systems. The flushing effect observed in the first period was probably due to the enhanced silicate weathering and sulfide oxidation accompanying intense soil erosion and mining disturbance.

Based on mass balance models, changing characteristics between the two periods for the total and each specific type of rock weathering were identified. The total chemical weathering rate and weathering rates of silicates, evaporites and sulfides (when assumed to exist) showed obvious decreases from the first period (high erosion period) to the second period (low erosion period). However, carbonate weathering rate did not change significantly, but had a slight increase in the

second period. This indicates the chemical weathering rates of evaporites, silicates and sulfides are more vulnerable to the impacts of physical weathering, while carbonate weathering rate is not distinctly affected by physical weathering.

The decreases of total dissolved solids and most of major ions between the two periods were found to coincide with the decrease of total suspended sediment. In addition, positive correlations were observed between some dissolved species concentration and suspended sediment in the first period, which had higher soil erosion rate. Both of the above observations suggest the impact of physical weathering on chemical weathering.

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