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SPECTRUM CHARACTERISTICS OF MAJOR ION CONCENTRATIONS AT WUHAN SECTOIN OF THE CHANGJIANG RIVER

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ABSTRACT: Spectrum analyses of water quality time series have been carried out for five hydrometric stations including Wuhan hydrometric station of the Changjiang (Yangtze) River, etc. The fluctuations of Ca^{2+}, Mg^{2+} and HCO_3^- concentrations in river water under different physical geography conditions have about two-year cycle which is corresponding to hydrometeorological quasi-biannual-oscillation (QBO). Na^+, Cl^- SO_4^{2-} have about two-year cycle in the area lightly affected by human activities while two-year cycle doesn't exist in the area heavily affected by human activities. All the fluctuations of major ions have about three-month cycle. The river discharge fluctuation accounts for 43.9%, 45.1%, 54.3%, 33.9%, 30.3% and 42.7% of the variance of Ca^{2+}, Mg^{2+}, HCO_3^-, Na^+, Cl^-, SO_4^{2-}, respectively, at Wuhan from 1962 to 1985. According to the spectrum characteristic of major ions, the duration of the time series has to be at least 13 years for trend analysis of monthly water quality data.

KEY WORDS: major ions; spectrum characteristic of water quality; water quality change; the Changjiang River

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1 INTRODUCTION

Since the 1930s, river water quality has been one of the main topics of water environmental sciences. Since the 1980s, global change has become the hot spot of earth science and environmental sciences, and global river water quality change has also been added to the contents of water quality research. Water quality study includes two aspects, i. e., river water quality characteristics and water quality change. So far, traditional water quality average based on time or discharge has been used to interpret water quality characteristics (SHEN, 1994). In fact, the temporal changes of water quality parameters have certain regular fluctuations with their own spectrum characteristic and causes. However, water quality average will lose this statistical information and can not comprehensively reflect the water quality characteristics. As to the study of water quality change, one of the main prerequisites is to determine how long of water quality time series is suitable for water quality trend research and can reflect the influence of human activity on water quality. Therefore, it is necessary for

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us to understand the natural fluctuation cycle of water quality and select proper duration of time series to study water quality change so as to deduct natural factors from the causes of water quality change.

So, the study on spectrum characteristics of river water quality is important for water quality research. But little attention has been paid to this topic around the world. This research project has adopted the method of spectrum analysis, which has been successfully used in the research of seismic hydrogeochemistry (HUANG, 1985; HUANG, 1989) to analyze the water quality time series of the Changjiang River at Wuhan Station and study the characteristics, cycles and causes of major ion fluctuation. The spectrum characteristics of major ions of the Changjiang River at Datong Station, the Xiangjiang River at Xiangtan Station, the Zhujiang(Pearl) River at Boluo Station and the Songhua River at Jiamusi Station is also studied in this research so as to understand the fluctuation characteristics of the major ions in river water under different regional environment conditions.

2 METHOD

In brief, if the time curve of water quality parameter is regarded as the superimposition of regular vibrations such as sine wave and cosine wave with different vibration frequencies as shown in formula (1), and the contributions of waves with different frequencies to the time series variance are compared, then, it is probably to get the main vibrations and their frequencies and cycles. The method that the time series of water quality parameters is analyzed in terms of frequency range is called spectrum analysis.

$$f(t) = \frac{a_0}{2} + \sum_{k=1}^{\infty}[a_k \cos(k\omega t) + b_k \sin(k\omega t)] \quad (1)$$

where $f(t)$ is time series of water quality parameter; a_k and b_k ($k = 0, 1, 2\ldots, b_0 = 0$), Fourier coefficient; k, wave number of interval harmonic component; ω, basic circular frequency, $\omega = 2\pi / T = 2\pi\nu$, T is basic cycle, ν is basic frequency.

2.1 Data Source

The water quality data of Wuhan Station and Datong Station of the Changjiang River, Xiangtan Station of the Xiangjiang River, Boluo Station of the Zhujiang River and Jiamusi Station of the Songhua River have been collected from the Water Year Book. All these monthly data were obtained based on the "Guidebook on Chemical Analysis of Inland Surface Waters" edited by Water Conservancy Ministry of China. The data were put into computer and the abnormal data were removed. Then, all the monthly data were centralized, and trend of the time series were deducted from the data series before spectrum analysis.

2.2 Harmonic Wave Analysis

According to formulas (2), (3) and (4), rectangular summation was used to calculate the Fourier coefficient of the time series of major ion concentrations, and the cycle analysis and forecast were also conducted.

$$a_0 = \frac{2}{N}\sum_{j=1}^{N} f_j \quad (2)$$

$$a_k = \frac{2}{N}\sum_{j=1}^{N} f_j \cos\frac{2\pi k(j-1)}{N} \quad (3)$$

$$b_k = \frac{2}{N}\sum_{j=1}^{N} f_j \sin\frac{2\pi k(j-1)}{N} \quad (4)$$

where k is wave number; N, time series number.

2.3 Power Spectrum Analysis

Power spectrum comes from the corresponding concept of physics. It is used to test the significance of vibration cycles. The indirect calculation method of power spectrum was applied in this research project, and the maximum time delay was $N/3$. Procedure compiled with computer was used to analyze the power spectrum of the centralized time series of monthly major ion concentrations of river water, obtaining the power density spectrum of major ions. The main cycles were determined based on the significance test of cycle.

2.4 Cross Spectrum Analysis

Cross spectrum analysis is used to study the relationship between two time series at a certain cycle. Since major ion concentrations are more or less influenced by river flow, the cross spectrum between the major ions and river flow were analyzed. Their condensation spectrum and phase spectrum were obtained to analyze the causes of the main cycles.

3 CYCLE ANALYSIS OF TIME SERIES OF MAJOR ION CONCENTRATIONS

3.1 Harmonic Wave Analysis

Concentrations of Ca^{2+} at Wuhan Station of the Changjiang River were used as an example to discuss the results of the harmonic wave analysis. The amplitude of Ca^{2+} concentration vibration decreased with the increase of wave number. The variance of Ca^{2+} concentration time series was $5.36(mg/L)^2$. According to formula (5), the wave numbers from 1 to 110 could fit 86.8% of the variance, and the fit series is nearly the same as the original series (Fig. 1). Therefore, the results of harmonic waves analysis showed that the time curve of Ca^{2+} concentration from 1962 to 1985 was the superimposition of a series of regular waves with different vibration frequency. Ca^{2+} concentration in 1986 was forecasted with the wave number from 1 to 110, and the result was in accordance with the monitored water quality.

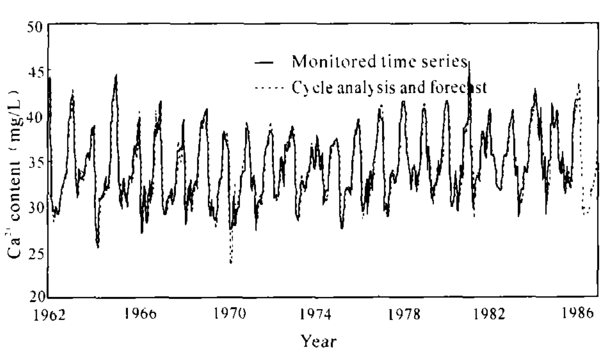

Fig. 1 The cycle analysis and forecast of Ca^{2+} concentration at Wuhan Station of the Changjiang River from 1962 to 1985

$$2\sigma^2 = \sum_{k=1}^{\infty} (a_k^2 + b_k^2) \quad (5)$$

where σ^2: the variance of the time series; a_k, b_k ($k = 0, 1, 2, b_0 \equiv 0$): Fourier coefficient; k: wave number of interval harmonic component.

3.2 Main Cycles and Cause Analysis

The contribution of waves with different vibration frequencies to the series variance differed from one to another. Power spectrum analysis of each major ion was conducted, and the results were shown as Table 1 and Fig. 2. The vibrations of Ca^{2+}, Mg^{2+} and HCO_3^- had an about two year significant cycle. According to formulas (5) and (6), the superimposition of amplitudes around the cycle of 21.33 months was estimated to be 1.09mg/L, and its contribution to the series variance was 11.1%.

Table 1 Main cycles of time series of major ion concentrations at Wuhan Station of the Changjiang River

	Ca^{2+}	Mg^{2+}	HCO_3^-	Na^+	Cl^-	SO_4^{2-}
Main cycles	21.33	21.33	21.33	48	64	64
(months)	2.7	2.7	2.7	2.7	2.7	2.7

$$\int_{\Delta l} s(l)dl \cong \frac{1}{2}(Al)^2 \quad (6)$$

where $s(l)$ is the power spectrum of wave with wave number of L; Al, the amplitude of wave with wave number of L.

Atmospheric sciences has shown that quasi-biannual-oscillation is one of the most important rules in the process of atmospheric recycle and key element change of climate (HUANG, 1988; WALSH and MOSTEK, 1980). Major ion concentrations are mainly affected by climate including rainfall and air temperature if the geological conditions are fixed. Air temperature affects the release rate of major ions from rock weathering. Rainfall influences the dilution of major ions in river water. So, quasi-biannual-oscillation of the key element of climate inevitably leads to the corresponding change of major ion concentrations in river water. Study has been carried out on the relationship between major ion concentrations and river discharge at Wuhan Station of the Changjiang River, and the results showed that the concentrations of Ca^{2+}, Mg^{2+} and HCO_3^- were greatly influenced by river flow and negatively correlated with river flow (Table 2). The

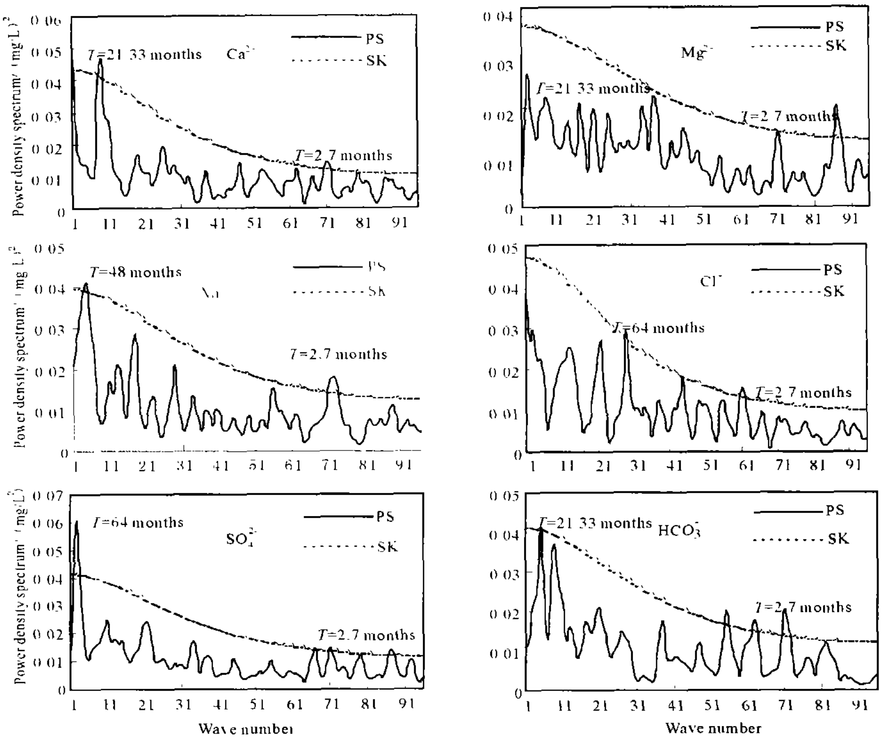

Fig. 2 Power spectrum of the time series of major ion concentrations at Wuhan Station from 1962 to 1985
PS: power density spectrum, SK: "red sound" spectrum

cross spectrum analysis between Ca^{2+}, Mg^{2+} and HCO_3^- concentrations and river discharge also showed that their condensation spectrum at nearly two years (21.33 months) was significant (Fig. 3). The oscillation phase of Ca^{2+} lagged 2 - 3 days behind that of the river discharge, and the oscillation phase of HCO_3^- lagged about 12 days behind that of the river discharge. Therefore, the quasi-biannual-oscillation of hydrometeorology leads to an about two-year cycle of Ca^{2+}, Mg^{2+} and HCO_3^- concentrations in river water. The results of spectrum analysis about water quality at Datong station of the Changjiang River, Xiangtan Station of the Xiangjiang River, Boluo Station of the Zhujiang River and Jiamusi Station of the Songhua River also showed that the time series of Ca^{2+}, Mg^{2+} and HCO_3^- concentrations had about two-year cycle. Since these rivers are located in different geographical regions, the above mentioned results revealed that the time series of Ca^{2+}, Mg^{2+} and HCO_3^- concentrations in rivers under various geographical conditions all had about two-year cycle which tallied with the cycle of hydrometeological oscillation.

Table 2 The correlation coefficient between major ion concentrations and river discharge at Wuhan Station of the Changjiang River

Major ions	Ca^{2+}	Mg^{2+}	Na^+	Cl^-	SO_4^{2-}	HCO_3^-
$r(\log Q \sim C)$	-0.76	-0.77	-0.26	-0.35	-0.64	-0.75
Sample number	307	307	303	305	302	307
Significant level	0.01	0.01	0.01	0.01	0.01	0.01

Q: river discharge; C: concentration of major ions in river water (mg/l); r: correlation coefficient

The oscillation of Na^+, Cl^- and SO_4^{2-} concentrations at Wuhan Station and Datong Station of the Changjiang River, Jiamusi Station of the Songhua River did not have about two-year cycle, while the oscillation of Na^+, Cl^- and SO_4^{2-} concentrations at Xiangtan Station of the Xiangjiang River and Boluo Station of the Zhujiang River have about two-year cycle. The water quality at Xiangtan Station and Boluo Station was less affected by human activities when compared to Wuhan Station. So, Na^+, Cl^- and SO_4^{2-} concentrations of river water in the areas heavily influenced by human activities did not have about two-year cycle, which reveals that

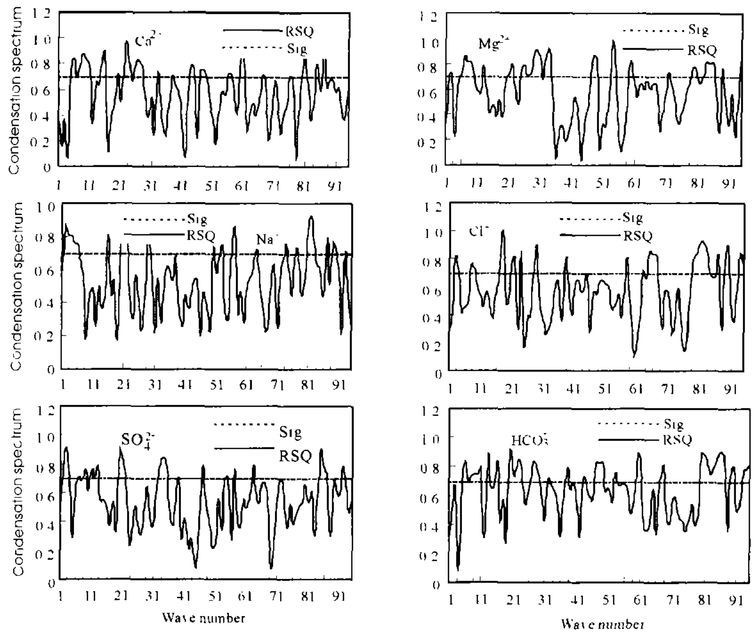

Fig. 3 The cross spectrum analysis between Ca^{2+}, Mg^{2+}, Na^+, Cl^-, SO_4^{2-}, HCO_3^- concentrations and river discharge at Wuhan Station of the Changjiang River from 1962 to 1985

RSQ: condensation spectrum; Sig: 0. 05 incredibility

the effects of human activities on water quality have concealed the effects of natural factors on water quality in these areas. While in the areas which were insignificantly affected by human activities, the concentrations of Na^+, Cl^- and SO_4^{2-} in river water had about two-year cycle.

Time series of all the major ion concentrations in the five studied stations had about three-month cycle. As to the Wuhan Station, the amplitude superimposition of Ca^{2+} concentration time series was estimated to be 0. 72mg/L at around three-month cycle, which covered 4. 8% of the variance of Ca^{2+} concentration time series. The three-month cycle of the major ion vibration might be related to the seasonal variation of hydrometerology. However, the time series of river discharge did not have three-month cycle at Wuhan Station, and the vibrations of major ion concentrations were not significantly in accordance with that of river discharge at this cycle. So it was inferred that the three-month cycle of the major ion concentration vibration was not caused by seasonal difference of water flow but other seasonal factors.

The research on groundwater has shown that the groundwater level has 11-year cycle which conforms to the cycle of sun spot(Department of Scientific Monitor of State Administration of Seimism of China, 1995). According to the above mentioned research, major ion concentrations of river water will also have 11-year cycle. The reason why it was not found in this research was that the time series of water quality was not long enough. The 11-year cycle is the longest cycle among what have been found to influence river water quality so far. If we want to study water quality change, it is necessary to determine how long duration of water quality data could cover the effects of this natural cycle on water quality and reflect the effects of human activities on water quality. According to Seasonal Kendall Test (HIRSCH, 1982), if water quality is monitored monthly, water quality tendency caused by 11-year cycle will not be significant when the duration is longer than 13 years. That is to say, KNUTSSON has pointed out, that water quality duration longer than 15 years is suitable for trend analysis (KNUTSSON, 1994), but this is the author's estimation based on groundwater vibration.

4 THE CAUSES OF VIBRATION

The cross spectrum analysis between major ion concentrations and river discharge at Wuhan Station showed that some vibration of major ions were related to river discharge and some were not related to river discharge(Fig. 3). According to the results of cross spectrum analysis and harmonic wave analysis, the contribution of river discharge vibration to the variance of major ion concentration duration was calculated based on formula (5) and (6). As shown in Table 3, most of the variance of time series of major ion concentrations was not caused by river discharge but air temperature and other factors. The contribution of river discharge to the variance of Ca^{2+}, Mg^{2+}, HCO_3^- and SO_4^{2-} concentrations was relatively large while that to the variance of Na^+ and Cl^- concentrations was relatively small, which accorded with the correlation coefficient between major ion concentrations and river discharge as shown in Table 2. River discharge made a larger contribution to the variance of major ion time series when the coefficient increased.

Table 3 Contribution of river flow to the variance of time series of centralized monthly major ion concentrations at Wuhan Station from 1962 to 1985

	Ca^{2+}	Mg^{2+}	HCO_3^-	Na^+	Cl^-	SO_4^{2-}
Variance $(mg/L)^2$	5.35	0.873	98.85	2.689	1.562	6.227
Selected wave number for harmonic wave analysis	1 - 145	1 - 144	1 - 145	1 - 145	1 - 145	1 - 145
Fit variance of the selected wave number	5.35	0.873	98.66	2.682	1.558	6.21
Contribution of river discharge to the variance						
Variance $(mg/L)^2$	2.350	0.394	53.65	0.912	0.474	2.662
Contribution(%)	43.9	45.1	54.3	33.9	30.3	42.7
Contribution of other factors to the variance						
Variance $(mg/L)^2$	3.349	0.479	45.20	1.777	1.088	3.565
Contribution(%)	56.1	54.9	44.7	66.1	69.7	57.3

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