

The water quality status of the estuary of Yellow River and its changing trend in the future

Li Liyang Fengchen Guozhen Wangxia Lihua

(Yellow River Basin Water environmental monitoring center, Zhengzhou 450004)

(Corresponding author: liliyang88888@hotmail.com)

Abstract: along with the theory of maintaining the healthy life of the Yellow River brought up and the rising of construction of wetland, the water quality status in Yellow River estuary and its trend of development in the future should be paid highly attention to, because in a sense the water quality status in the estuary is directly related to the continuation of the Yellow River's healthy life in the future, as well as the ups and downs of the wetland construction in the estuary. Combining the results of analysis and assessment of the water quality at LiJin Station in the Yellow River's estuary in "Yellow River basin water resources bulletin", this paper has generalized the water quality status in the Yellow River estuary at present. Further more combining the field data of mainly water quality parameters at LiJin Station from 1996 to 2005, the trend of the fluctuation of water quality at the estuary has been carried out on both qualitative and quantitative analysis by using the Seasonal Kendall trend test, which will be useful for the reference to management.

Key words: Seasonal Kendall test; Yellow River estuary; Water quality status; fluctuation trend

Introduction

In recent years along with the theory of maintaining the Yellow River healthy life brought out and the rising of construction of wetland at Yellow River estuary, the water quality status becomes more and more important for in a sense it is direct relation to the maintenance of the Yellow River healthy life and its ups and downs of the wetland constructions at estuary. Therefore it is imperative to research the water quality status and its fluctuating trend at the Yellow River estuary.

1 Water quality status at Yellow River estuary in recent years

Presently there is only one water quality station, LiJin station, at the estuary of the Yellow River, therefore the water quality of LiJin station basically reflects the water quality of the Yellow River estuary. According to the analytic and overall assessment results of the water quality at LiJin station on 'Yellow River basin water resources bulletin' from 2003 to 2005 (see table 1), it can be

seen that on some extent the water quality has become better than before. The water quality of the estuary in 2005 belongs to class three, which has reached to the drinking water quality requirement of surface water and was better than class four of 2003 and 2004's. At the same time the organic contamination in low water period also weaken, the concentrations of the primary pollution parameters , such as chemical oxygen demand (CODCr),have cut down to the drinking water quality requirement.

From the status of every month in a year, the water quality status is different in some extent between each month. According to the assessment results of every month on 'the Yellow River basin water resources quality bulletin' in 2005,the water quality is poor at the beginning of flood season and some month of low water period (see table 2),the over limit rate reaches 33.3 percent. The primary pollution items are ammonia nitrogen, CODcr and petroleum.

Table 1 the water quality status of the Yellow River estuary in recent three years

Year	Water period	Water quality class	Primary overproof items
2003	Low water period	IV	COD
	Flood period	III	
	Whole year	IV	COD
2004	Low water period	III	
	Flood period	IV	petroleum
	Whole year	IV	Petroleum
2005	Low water period	III	
	Flood period	III	
	Whole year	III	

Table 2 Every month water quality status at Yellow River estuary in 2005

month	Water quality class	Primary over- proof items	month	Water quality class	Primary over proof items
Jan	III		Jul	IV	COD、 Petroleum
Feb	III		Aug	IV	COD
Mar	IV	ammonia nitrogen	Sept	III	
Apr	IV	Petroleum	Oct	III	
May	III		Nov	III	

Jun	III		Dec	III	
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2. Analysis of water quality fluctuation trend at Yellow River estuary

2.1 Determination of the analytic method and selection of water quality parameters

There are two kinds of water quality fluctuation trend analysis in stream, one is to model the water quality according to the field data in the past, which is used to deduce the water quality trend of development in the future, and it is also called water quality prediction. The other is to analyse the water quality change during the past to now according to the water quality series. The second case was considered in this paper. The water quality series of 1998 to 2005 at LiJin station was used, and eight water quality parameters were chosen, which include total hardness, chloride, sulfate, ammonia nitrogen, permanganate index, COD_{Cr}, BOD₅, petroleum.

Because the natural water quality data are random, seasonal, and relative, the routine parametric test methods, such as linear regression test, T test, analysis of variance and multivariable normal method, cannot completely meet the feature of the water quality series. So the water quality trend analysis is drawback when these methods are used. Combining the characters of water quality data, statistician named G. Kendall has brought up a more suitable and rational nonparametric test--Seasonal Kendall test.

2.2 Theory of seasonal Kendall test

2.2.1 The Kendall t test

The theory of the seasonal Kendall test is that let the water quality data in the same month or season of every year to compare with each other, and that if the later value (increasing values in time) is bigger than the former, we will record it as "+", else as "-". If the number of the "+" is bigger than the "-", it is likely upward trend, similarly if the number of the "-" is smaller than the "+", the likely trend is downward and if the two are equal, the trend is null.

According to the seasonal Kendall test, the null hypothesis H₀ is that the random variables is independent of the time, presume that there are the same probability distribution in the water quality data of the whole twelve months.

Suppose the series x of the observed water quality data in the n years and p months as follow,

$$x = \begin{bmatrix} x_{11} & x_{12} & \cdots & x_{1p} \\ x_{21} & x_{22} & \cdots & x_{2p} \\ \cdots & \cdots & \cdots & \cdots \\ x_{n1} & x_{n2} & \cdots & x_{np} \end{bmatrix}$$

In the formulae the data (X_{11}, \dots, X_{np}) are the observed value of the water quality concentrations in every month.

(1) To the case of the i th among the p months ($i \leq p$)

Let the sum of the signs of the "+" and "-" which is from the compared water quality series in the i th month of every year equal to the S_i , and the number of data group which can be compared D -value in the i th month equal to m_i . Under the null hypothesis the random series, S_i , approximately submits to the normal distribution, then the expectation and variance of S_i are as follows,

$$\text{Expectation: } E(S_i) = 0$$

$$\text{Variance: } \sigma_i^2 = \text{Var}(s_i) = n_i(n_i - 1)(2n_i + 5)/18$$

When there are t same numbers in the n_i no-missing-value, the formulae σ_i^2 is as follow,

$$\sigma_i^2 = \text{Var}(s_i) = \frac{n_i(n_i - 1)(2n_i + 5)}{18} - \frac{\sum_t t(t - 1)(2t + 5)}{18}$$

(2) The total case of the p months

$$\text{Let } S = \sum_{i=1}^p S_i \quad M = \sum_{i=1}^p m_i$$

Under the null hypotheses the mean and variance of S in the P months are as follow,

$$\text{Mean: } E(s) = \sum_{i=1}^p E(s_i) = 0$$

$$\text{Variance: } \sigma^2 = \text{Var}(s) = \sum_{i=1}^p \frac{n_i(n_i - 1)(2n_i + 5)}{18}$$

When there are t same numbers in the water quality series of the n years, namely

$$\text{Var}(s) = \sum_{i=1}^p \frac{n_i(n_i - 1)(2n_i + 5)}{18} - \frac{\sum_t t(t - 1)(2t + 5)}{18}$$

Kendall found that when $n \geq 10$, S also takes on the normal distribution, and the standard variance, z , is as follow,

$$z = \begin{cases} \frac{s-1}{[Var(s)]^{1/2}}, & \text{当 } s > 0 \\ 0, & \text{当 } s = 0 \\ \frac{s+1}{[Var(s)]^{1/2}}, & \text{当 } s < 0 \end{cases}$$

(3) The trend test

The Kendall test's tau be defined as $T = s/m$, therefore in the two-side trend test ,if $|z| \leq \alpha/2$, we accept the null hypothesis. Where $FN(Z\alpha/2) = \alpha/2$, FN being the standard normal cumulative distribution function, namely:

$$FN = \frac{1}{\sqrt{2\pi}} \int_{|z|}^{\infty} e^{-\frac{1}{2}t^2} dt$$

α being the size of the significance level for the trend test, it's value is as follow

$$\alpha = \frac{2}{\sqrt{2\pi}} \int_{|z|}^{\infty} e^{-\frac{1}{2}t^2} dt$$

We take the significance level α as 0.1 and 0.01, that is, when $\alpha \leq 0.01$, the test has the highly significant level, and when $0.01 < \alpha \leq 0.1$, the test is significant, when the results of α meet the upper two conditions, t value is positive, it indicates that there is a prominent or highly significant upward trend, when the t value is negative, it indicates that there is a prominent or highly significant downward trend, and when the t value is null, it indicates no trend.

2.2.2 Seasonal Kendall slope estimate

The Seasonal Kendall slope is expressed with the slope of the linear regression, which reflects the size of trend. It is defined as the median of the whole quotients between the D-value of compared two numbers and the discrepant year number of them in the test. The estimated value of the slope only illustrates the mean annual situation of concentration change of water quality in the test year.

The estimated value of the trend slope was defined as follow:

To all X_{ij} , X_{ik} ($i=1,2,\dots,p$, $j=1,2,\dots,n$), the slope of two random numbers in the water quality series in month i th is defined as d_{ijk} . Because $d_{ijk} = (X_{ij} - X_{ik}) / (j - k)$ ($1 \leq k < j \leq n$), the estimated value of trend slope, B , is equal to the median of all the d_{ijk} . when $S > 0$, $B \geq 0$; when $S < 0$, $B \leq 0$. So B is not affected by the extreme value or singularity in the water quality series. Also it is not affected by season.

2.2.3 Flow adjustment concentration test

The flow adjustment concentration test is to judge whether the pollutant concentration change in the stream is caused by discharge variation or not by using the residual analysis.

(1) In order to seek the best relation with the linear regression analysis, the formula of flow adjustment is as follow:

$$\hat{c} = a + b \cdot c(Q)$$

Where is \hat{c} the estimated concentration, Q the flow in step with concentration, $c(Q)$ the function based on flow variation, and a, b the coefficient.

When the pollutants in the stream come from the point source load, it is diluting effect, and described as the following equations:

$$\textcircled{1} \quad c(Q) = \lambda_1 + \lambda_2 \frac{1}{Q} + \varepsilon$$

$$\textcircled{2} \quad c(Q) = \lambda_1 + \lambda_2 \frac{1}{1 + \lambda_3 Q} + \varepsilon$$

Where is ε the error taken on zero mean, $\lambda_1, \lambda_2, \lambda_3$ —coefficient ($\lambda_1, \lambda_2 \geq 0, \lambda_3 > 0$).

When the pollutants in the stream come from non-point pollution, the relation between concentration and flow can be expressed as follow:

$$\textcircled{3} \quad C(Q) = \lambda_1 + \lambda_2 Q + \lambda_3 Q^2 + \varepsilon$$

$$\textcircled{4} \quad C(Q) = \lambda_1 + \lambda_2 \ln Q + \varepsilon$$

In the formula the meaning of the signs is same as the above.

According to the series of concentration and flow, the a, b in the equation of linear regression, $\hat{c} = a + b \cdot c(Q)$, are estimated respectively, and R^2 is calculated, which reflects the parameter of correlativity.

Among the four calculated regression equation, the one which has the maximal R^2 was chosen. At the same time the regression test was carried out to the chosen curve.

(2) The residual series of W_{ij} of the flow adjustment concentration, which is the difference of measured value and the expected value of the estimated value, W_{ij} was calculated by using the accepted equation.

(3) The confidence of α and slope of B of the series of W_{ij} were got by using the seasonal Kendall test, which can be used to judge the trend of flow adjustment concentration.

2.3 Interpretation of results

The mainly eight water quality parameters of actual water quality monitoring data from 1996 to 2005 at LiJin station have been calculated by the professional water quality trend (PWQTrend) software which is based on the method of the flow adjustment Seasonal Kendall test. The results are shown in table 3.

As shown in table 3, the water quality parameters of sulfate, ammonia nitrogen, permanganate index, chemical oxygen demand(COD_{Cr}), five day biologic oxygen demand (BOD₅) show highly significant downtrend or prominent downtrend; Petroleum shows prominent uptrend; Total hardness and chloride show no any distinct trend, Which illustrate that except petroleum, the water quality pollution in the Yellow River estuary has lessened in recent decade, and the controlling of pollution has got some good results.

Table 3 the outcome of water quality trend analysis of the LiJin station at the Yellow River estuary.

Analytic items	Trend of concentration	Trend of flux	Flow adjustment		
			Type of formula	B (mg/L/a)	Trend
Total hardness	—	↑	$\ln(C)=a+b*(\ln(Q)+B*\ln(Q)*\ln(Q))$	3.56	↑
Chloride	—	↑↑	$C=a+b*(1/(1+B*Q))$	1.23	—
Sulfate	↓↓	↑↑	$C=a+b*(1/(1+B*Q))$	-3.72	↓
Ammonia nitrogen	↓↓	↑	$C=a+b*(1/(1+B*Q))$	-0.0143	—
COD _{Mn}	↓	↑↑	No Suitable Formula for Adjustment	-0.067	↓
COD _{Cr}	↓↓	↑	$C=a+b*(1/(1+B*Q))$	-1.91	↓↓
BOD ₅	↓	↑↑	No Suitable Formula for Adjustment	0	↓
Petroleum	↑	↑↑	No Suitable Formula for Adjustment	0	↑

Note: (1)The sign of "↑" stands for prominent uptrend, "↑↑" highly significant uptrend, "↓" prominent downtrend, "↓↓" highly significant downtrend, and "—" no trend;

(2)COD_{Mn} stands for permanganate index.

It can be seen from the flux trend that eight water quality parameters indicate uptrend or highly significant uptrend. Combining the outcome of the water quality concentration trend analysis, it is illustrated that the total quantity of all pollutants in the estuary has been increased because of the increase of discharge.

From the trend analysis of flow adjustment, it has shown uptrend for total hardness and petroleum, while downtrend or highly significant downtrend for sulfate, permanganate index, chemical oxygen demand, Five day BOD, and no trend for chloride and ammonia nitrogen. Combining the different formula style of every water quality parameter, it is indicated that total

hardness give priority to non-point pollution, while others give priority to point source pollution. Based on the feature of downstream channel, which is belong to over ground river, it is shown that the water quality pollution in the estuary mainly come from the drain in the upper or middle course. So the harness of point source is still an emphasis. In addition, it is need to explain that there are no flow adjustment formula styles for minor water quality parameter because the negative correlation between concentration and flow is intricate, and it is difficult to find the well-formed formula style, it should be thought as point source pollution.

3 . Conclusion

(1) In recent years the water quality in the Yellow River estuary has become better than before, and the average water quality in 2005 has reached the requirement of drinking water of surface water, although there are still some months whose water quality is overproof.

(2) The water quality concentration trend analysis in recent decade has shown that except the petroleum which has still showed uptrend, the others have shown prominent downtrend or highly significant downtrend.

(3) The flux trend analysis shows that because the water inflow has increased in recent years, the overall pollutants which mainly come from the upper and middle river have increased.

(4)The trend analysis of flow adjustment shows the pollution in the estuary give priority to point source pollution, whose pollutant source mainly come from the drain in the upper and middle course, therefore the strengthen harness in the drain is still an emphases in the future.

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黄河河口段水质状况及变化趋势分析

李立阳 冯晨 郭正 王霞 李娅

(黄河流域水环境监测中心 郑州 450004)

摘要: 随着“维持黄河健康生命”理论的提出及河口湿地建设的兴起,黄河河口段水质状况及未来发展趋势引起人们的高度关注。从某种意义上来说,河口段的水质状况直接关系到未来黄河健康生命的维持以及河口湿地建设的成败。本文结合近年来《黄河流域水资源公报》对黄河河口段利津站的水质评价结果,归纳出目前黄河河口段水质状况。在此基础上,结合1996-2005年利津站主要水质参数的实测资料,运用季节性肯达尔检验对河口段水质变化趋势进行定性与定量分析,并通过流量调节浓度检验判断浓度趋势的来源,对管理部门具有重要的参考价值。

关键词: 季节性肯达尔检验 黄河河口段 水质状况 变化趋势

引言

近年来,随着“维持黄河健康生命”理论的提出及河口湿地建设的兴起,黄河河口段水质状况显得尤为重要。从某种意义上来说,河口段的水质状况及未来变化趋势直接关系到黄河健康生命的维持以及河口湿地建设的成败。因此,研究黄河河口段的水质状况及未来变化趋势就显得尤为必要。

1 近年黄河河口段水质状况

目前在黄河干流河口段只设定一个重要的入海水质把口站——利津站,因此利津站的水质状况就基本反映了黄河河口段的水质状况。根据2003年至2005年《黄河流域水资源公报》对利津段水质综合评价分析结果(见表1),可以看出,近三年河口段水质状况有一定好转,全年平均水质已从2003年、2004年IV类水好转为2005年的III类水,达到地表水饮用水水质要求。同时枯水期的有机污染也有所减弱,主要污染指标化学需氧量(COD)含量已降到饮用水水质要求。

从年内来看,各月水质状况略有不同。根据2005年各月《黄河流域水资源质量公报》评价结果,在汛期初期及枯水期的部分月份水质较差(见表2),超标率达33.3%。主要污染项目是氨氮、COD和石油类。

表 1 近三年黄河河口段水质状况

年 份	水 期	综合水质类别	主要超标项目
2003	枯水期	IV	COD
	丰水期	III	
	全年	IV	COD
2004	枯水期	III	
	丰水期	IV	石油类
	全年	IV	石油类
2005	枯水期	III	
	丰水期	III	
	全年	III	

表 2 2005 年各月黄河河口段水质状况

月份	水质类别	主要超标项目	月份	水质类别	主要超标项目
1	III		7	IV	COD、石油类
2	III		8	IV	COD
3	IV	氨氮	9	III	
4	IV	石油类	10	III	
5	III		11	III	
6	III		12	III	

2、黄河河口段水质变化趋势分析

2.1 分析方法的选定及水质参数的选择

河流水质趋势分析有两种：一种是根据过去实测水质资料进行模拟建模，由模型推断未来水质的发展趋势，也称水质预测；一种是由过去至现在的水质序列分析其间水质发生的变化。本文主要是考虑后一种情形。采用利津站 1996-2005 年的水质序列，选择总硬度、氯化物、硫酸盐、氨氮、高锰酸盐指数、化学需氧量(COD)、五日生化需氧量（B O D₅）、石油类等 8 个主要水质参数进行趋势分析。

由于天然水质数据具有随机性、季节性、相关性等特点，常规的参数检验方法，如线性

回归检验、t 检验、方差分析及多变量正态法检验等都不能很好地满足水质序列的特点，因此使用这类方法在水质趋势分析中遇到了障碍。结合水质数据的特征，统计学家 G·Kendall 提出了一种更为广泛适用、合理的非参数检验—季节性肯达尔检验。

2.2 季节性肯达尔检验原理

2.2.1 肯达尔 t 检验

季节性肯达尔检验的原理是将历年相同月(季)的水质资料进行比较，如果后面的值(时间上)高于前面的值记为“+”号，否则记作“-”号。如果加号的个数比减号的多，则可能为上升趋势，类似地，如果减号的个数比加号的多，则可能为下降趋势，如果相等则为无趋势。

零假设 H_0 为随机变量与时间独立，假定全年 12 个月的水质资料具有相同的概率分布。

设有 n 年 P 月的水质资料观测序列 x 为

$$x = \begin{bmatrix} x_{11} & x_{12} & \cdots & x_{1p} \\ x_{21} & x_{22} & \cdots & x_{2p} \\ \cdots & \cdots & \cdots & \cdots \\ x_{n1} & x_{n2} & \cdots & x_{np} \end{bmatrix}$$

式中， x_{11}, \cdots, x_{np} 为月水质浓度观测值。

(1) 对于 P 月中第 i 月 ($i \leq P$) 的情况

令第 i 月历年水质系列相比较(后面的数与前面的数之差)的正负号之和为 S_i ，第 i 月内可以作比较的差值数据组个数为 m_i ，则在零假设下，随机序列 $S_i (i=1, 2, \cdots, p)$ 近似地服从正态分布，则 S_i 的均值和方差如下：

均值： $E(S_i) = 0$

方差： $\sigma_i^2 = \text{Var}(s_i) = n_i(n_i - 1)(2n_i + 5)/18$

当 n_i 个非漏测值中有 t 个数相同，则公式 σ_i^2 为

$$\sigma_i^2 = \text{Var}(s_i) = \frac{n_i(n_i - 1)(2n_i + 5)}{18} - \frac{\sum_i t(t-1)(2t+5)}{18}$$

(2) 对于 P 月份总体情况

$$\text{令 } S = \sum_{i=1}^p S_i \quad m = \sum_{i=1}^p m_i,$$

在假设下， P 月 S 的均值和方差为

$$\text{均值: } E(s) = \sum_{i=1}^p E(s_i) = 0$$

$$\text{方差: } \sigma^2 = \text{Var}(s) = \sum_{i=1}^p \frac{n_i(n_i - 1)(2n_i + 5)}{18}$$

当n年水质系列有t个数相同时，同样有：

$$\text{Var}(s) = \sum_{i=1}^p \frac{n_i(n_i - 1)(2n_i + 5)}{18} - \frac{\sum_i t(t-1)(2t+5)}{18}$$

肯达尔发现，当n≥10时，S也服从正态分布，并且标准方差Z为

$$z = \begin{cases} \frac{s-1}{[\text{Var}(s)]^{1/2}}, & \text{当 } s > 0 \\ 0, & \text{当 } s = 0 \\ \frac{s+1}{[\text{Var}(s)]^{1/2}}, & \text{当 } s < 0 \end{cases}$$

(3) 趋势检验

肯达尔检验统计量t定义为： $t=S/m$ ，由此在双尾趋势检验中，如果 $|Z| \leq Z_{\alpha/2}$ ，则接受零假设。这里 $FN(Z_{\alpha/2}) = \alpha/2$ ，FN为标准正态分布函数，即：

$$FN = \frac{1}{\sqrt{2\pi}} \int_{|z|}^{\infty} e^{-\frac{1}{2}t^2} dt$$

α 为趋势检验的显著水平， α 值为

$$\alpha = \frac{2}{\sqrt{2\pi}} \int_{|z|}^{\infty} e^{-\frac{1}{2}t^2} dt$$

我们取显著性水平 α 为0.1和0.01，即当 $\alpha \leq 0.01$ 时，说明检验具有高度显著性水平，当 $0.01 < \alpha \leq 0.1$ 时，说明检验是显著的，当 α 计算结果满足上述二条件情况下，当t为正时，则说明具有显著（或高度显著性）上升趋势，当t为负时，则说明具有显著（或高度显著性）下降趋势，当t为零时，则无趋势。

2.2.2 季节性肯达尔斜率估计

季节性肯达尔斜率是用线性回归的斜率表示，反映趋势大小。定义为：在进行该检验中所有被比较的两数的差值除以两数间相差的年数的商的中值。该斜率估值只说明历年来水质浓度变化的年平均情况。

趋势斜率估值B的确定：对所有 X_{ij} ， X_{ik} ($i=1, 2, \dots, p$, $j=1, 2, \dots, n$)，第i月水质序列任意

两数的斜率为 d_{ijk} 。由于 $d_{ijk} = (X_{ij} - X_{ik}) / (j - k)$ ($1 \leq k \leq j \leq n_i$)，p个月的情况为 $d = \sum_{i=1}^p d_{ijk}$ ，

则趋势斜率估值B为所有 d_{ijk} 的中值，当 $S > 0$ 时， $B \geq 0$ ； $S < 0$ 时， $B \leq 0$ 。这样B不受水质序列中极值（奇异点）的影响，季节性也对B无影响。

2.2.3 流量调节浓度检验

流量调节浓度检验即通过残差分析来判断水质趋势是否是由于流量变化引起河流中污

染物浓度的变化。

(1) 用线性回归分析来寻求最适合的关系，流量调节方程的形式为：

$$\hat{c} = a + b \cdot c(Q)$$

其中： \hat{c} — 估计浓度； Q —与浓度同步流量； $c(Q)$ — 以流量为变量的函数； a 、 b — 系数

当河流中染污物来源于点源负荷时，是稀释作用，可用下面的方程来描述：

$$\textcircled{1} \quad c(Q) = \lambda_1 + \lambda_2 \frac{1}{Q} + \varepsilon$$

$$\textcircled{2} \quad c(Q) = \lambda_1 + \lambda_2 \frac{1}{1 + \lambda_3 Q} + \varepsilon$$

式中： ε —具有零均值的误差； λ_1 ， λ_2 ， λ_3 —系数（ λ_1 ， $\lambda_2 \geq 0$ ， $\lambda_3 > 0$ ）

当河流中污染物来源于面源污染时，可用下式来表示浓度流量间的关系：

$$\textcircled{3} \quad C(Q) = \lambda_1 + \lambda_2 Q + \lambda_3 Q^2 + \varepsilon$$

$$\textcircled{4} \quad C(Q) = \lambda_1 + \lambda_2 \ln Q + \varepsilon$$

式中的符号意义同前述。

根据浓度和流量系列，分别估计线性回归方程 $\hat{c} = a + b \cdot c(Q)$ 中的 a 、 b ，计算 R^2 （反映相关程度的参数）。

从求得4个回归方程，选择 R^2 最大的一个流量调节方程，即拟合最佳的曲线，同时，对所选曲线进行回归检验。

(2) 以接受检验的方程，计算流量调节浓度的残差系列 W_{ij} （实测值与估计值望值之差）。

(3) 将系列 W_{ij} 运用季节性肯达尔检验求得置信度 a 和斜率 B ，即可判断流量调节浓度趋势。

2.3 结果分析

对利津站 8 个主要水质参数 1996-2005 年的实测水质监测资料，运用 PWQTrend (professional water trend) 水质趋势分析软件(基于流量调节的季节性 Kendall 检验方法) 进行计算，结果如表 3。

从表 3 可以看出，水质浓度趋势中，硫酸盐、氨氮、高锰酸盐指数、化学需氧量(CODCr)、五日生化需氧(BOD5)呈高度显著下降趋势或显著下降趋势；石油类呈显著上升趋势；总硬度及氯化物呈无明显升降趋势。说明近 10 年除石油外，黄河口段水体中其余的有机污染或无机污染已有所减轻，治污工作已取得一定成效。

从通量趋势来看，8 种参数全部呈上升趋势或高度显著上升趋势。结合水质浓度趋势分析结果，说明下游流量明显增大，导致输入河口段的污染物总量在增多。

表 3 黄河河口段利津站水质趋势成果表

分析项目	水质浓度趋势	通量趋势	流量调节		
			公式类型	B (mg/L/a)	趋势
总硬度	—	↑	$\ln(C)=a+b*(\ln(Q)+B*\ln(Q)*\ln(Q))$	3.56	↑
氯化物	—	↑↑	$C=a+b*(1/(1+B*Q))$	1.23	—
硫酸盐	↓↓	↑↑	$C=a+b*(1/(1+B*Q))$	-3.72	↓
氨氮	↓↓	↑	$C=a+b*(1/(1+B*Q))$	-0.0143	—
COD _{Mn}	↓	↑↑	无适合公式	-0.067	↓
COD _{Cr}	↓↓	↑	$C=a+b*(1/(1+B*Q))$	-1.91	↓↓
BOD ₅	↓	↑↑	无适合公式	0	↓
石油类	↑	↑↑	无适合公式	0	↑

注: (1) “↑”表中表示显著上升趋势;“↑↑”表示高度显著上升趋势;“↓”表示显著下降趋势;“↓↓”表示高度显著下降趋势;“—”表示无明显升降趋势

(2) COD_{Mn} 表示高锰酸盐指数.

从流量调节趋势分析结果来看,总硬度及石油类呈上升趋势,硫酸盐、高锰酸盐指数、化学需氧量、五日生化需氧量呈显著下降趋势或高度显著下降趋势,氯化物、及氨氮无明显升降趋势。结合各种水质参数的流量调节公式类型,可以看出,总硬度以面源污染为主,其余各项以点源污染为主。另外,根据下游河道地上河特点,说明河口段的水质污染主要来源于上、中游的排污口,点源治理工作仍是一个重点。最后,需要补充说明的是表中有少数水质参数出现无适当的流量调节公式类型,都是因为水质参数浓度与流量的负相关关系十分复杂,难以找到合适的公式类型,所以都应作点源污染处理。

3. 结论

(1)尽管年内仍有少数月份出现水质超标现象,黄河河口段水质状况近年来已有所好转,2005 年全年平均水质已达到地表水饮用水要求。

(2)近 10 年水质浓度趋势分析表明,除石油仍呈上升趋势外,其余各项有机和无机污染已呈明显下降趋势或高度显著下降趋势,水污染治理工作已初见成效。

(3)通量趋势分析表明,由于近 10 年下游来水量的增加,导致上、中游河段输入河口的污染物总量增多。

(4)流量调节趋势分析表明,河口段的水质污染以点源污染为主,其污染源主要来源于上、中游河段的排污口,因此,加强排污口的治理工作仍是今后工作的一个重点。

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