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Assessing the impact of leather industries on the quality of water discharged into the East China Sea from Wenzhou Watersheds

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Abstract

Ammonium nitrogen and total germanium are among the main pollutants in the wastewater discharged from the leather industry. The intake of high concentrations of ammonium nitrogen and/or total germanium harms human health and biological species, as is well documented in literature. This paper focuses on assessing the trends of ammonium nitrogen and total germanium concentrations through time in two watersheds (Aojiang and Oujiang) in the Wenzhou metropolitan area of Zhejiang Province and their relationships with the released wastewater using regression and correlation statistics. The paper also utilizes the integrated pollution index to evaluate water quality in the two watersheds. Preliminary results show that, from 1992 to 1998 in the Aojing watershed, the concentrations of ammonium nitrogen and total germanium increased 13 and 14 times, respectively, decreasing somewhat after 1998, while between 1992 and 1997 in the Oujiang watershed, the concentrations increased, then decreased after 1997. The concentrations of ammonium nitrogen and total germanium are positively related to the amount of released wastewater. The concentrations of ammonium nitrogen and total germanium exceeded water standards 12 and 3 times, respectively, in Pingyang county of the Aojiang watershed, 14 and 3.3 times in Lucheng District of the Oujiang watershed, and 14 and 3.8 times in the Ouhai Oujiang watershed, respectively. In Pingyang county of the Aojiang watershed, the water quality degraded from Type III in 1992 to over Type V in 2003, and in the Oujiang watershed, the water quality degraded from Type II to over Type IV in 1999, when they were compared with the water quality standards. The water quality slightly improved in 2003 for the Oujiang watershed. It appears that pollution did have a direct positive correlation with leather industry production in the Pingyang Aojing watershed, while there was a negative correlation between the two in the Oujiang watershed. In these two watersheds, the integrated pollution index did not appear to relate to population dynamics and agricultural production. This paper also discusses the current new methodologies and approaches adopted nationally and internationally to reduce the contaminants and purify the environment for maintaining a sustainable and healthier environment in Wenzhou.

Keywords: Watershed water quality; Ammonium nitrogen and germanium; Leather industry wastewater; Impact assessment; Ecological risks

1. Introduction

Higher living standards are likely to increase demand for natural leather products. Consequently, in recent decades, many small enterprises of the leather industry emerged in the towns of Shuitou, Lucheng and Ouhai in the Wenzhou metropolitan area of Zhejiang Province, China (Wenzhou Statistics Bureau, 2001). The increased number of leather industries in Wenzhou generated a large amount of wastewater carrying toxic contaminants that harm human and ecosystem health. Although the emerging leather industry stimulated the local economy (Wenzhou Statistics Bureau, 2001), the cost due to environmental pollution is unbearable (Wenzhou EMC, 2002; Hansell et al, 2003; Xie, 2004; Liu, 2005). In order to sustain the economic development, strategies and policy actions must be taken to balance industrial development, human health, and ecosystem health in the region. Among the contaminants,

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ammonium nitrogen (NH_4^+-N) and total germanium (Ge) are the main constituents in the wastewater released from the leather industry (Wenzhou EMC, 2002).

In recent years, there have been many studies linking these contaminants to ecosystem and human health issues. For instance, the impact of high concentrations of nitrate in drinking water has been documented to cause methemoglobinemia, or blue baby syndrome, a condition where nitrate interferes with the transport of oxygen in babies (Cooke and Kalita, 2002; Cébron et al., 2003; Skipton and Hay, 1998; Portage County Groundwater, 2004). Another study, conducted in 1997, reported that nitrate levels in excess of 4 mg NO_3^--N/L were found to be highly correlated with increased risk of non-Hodgkins lymphoma in rural areas (Cooke and Kalita, 2002). Similarly, germanium, a heavy metal that is known to irritate the eyes, the skin and the respiratory tract (Lide, 1998; Lenntech, 2004) has been shown to impact health. When present in blood, it may cause lesions in blood cells. Exposure to Ge may result in the death of various fish species (Lenntech, 2004). Wang and Ding (2002) reported that the intake of high concentrations, 0.015–0.033 mg/m^3, of Ge could cause a variety of harm to the human body, from causing protein fixation and over-stimulating the digestion system, all the way to causing lung cancer.

High concentrations of NH_4^+-N and Ge have severely impacted local ecosystem and human health (Xie, 2004; Liu, 2005). According to the news media network, Xie (2004) and Liu (2005) reported that in the town of Shuitou, located in the Aojiang watershed in the Wenzhou metropolitan area, the crops had low yields, the air was full of bad odors, and water was contaminated. Strange diseases were prevalent and few young people could pass physical exams for military admission. Although these phenomena could be due to integrated effects of pollution in the region, the reduction of the NH_4^+-N and Ge pollutants in water bodies appeared to be a worthwhile and urgent environmental goal.

Therefore, the objectives of the study are to examine the concentrations of NH_4^+-N and Ge in the released wastewater, to assess the water quality in the Aojiang and Oujiang watersheds in the Wenzhou metropolitan area, and to understand the impact of these pollutants on human and ecosystem health in the watershed and the surrounding ocean. Finally, the paper proposes mitigation alternatives to clean up contaminated areas and preventative methods to control pollution sources.

2. Materials and methods

2.1. Study site

The Aojiang and Oujiang watersheds, two of the four major watersheds releasing water to the open sea, were selected for this study. Both watersheds are located in the Wenzhou metropolitan area of Zhejiang Province. The Aojiang watershed is located in the southern part of Wenzhou. It originates from the town of Shuitou in Pingyang County (Fig. 1), covers 82 km in length, runs through the towns of Shuitou, Xiaojiang, Aojiang and Longgang, and finally releases water into the Aojing Ocean. Among these towns, the leather industry is mostly concentrated in Shuitou, the headwater area of the watershed.

The Oujiang watershed is located in the middle part of Wenzhou, with the second largest river running through the Wenzhou metropolitan area. The 388 km long river originates from Bai Shan Zu in Qingyuan County and passes through the Lishui metropolitan area and the counties of Yong Jia and Leqing, Lucheng, Longwan and Ouhai (Fig. 1). Among the counties and towns that the river runs through, Ouhai and Lucheng have the highest concentration of the leather industry. Since this study focuses on water quality impact from leather industry wastes, the study uses the data from Pingyang County to represent the Aojiang watershed, and the data from Lucheng and Ouhai to represent the Oujiang watershed.

Using the national standards for determining the surface water quality functions (National EPA, 1997), Wenzhou Environmental Protection Bureau assigned the surface water quality as Type III for the Aojiang watershed and Types II–III (Table 1) for the Oujiang watershed in 1992. Although the two watersheds cover the counties and towns mentioned above, the study focused on the towns with the most leather industry activities.

2.2. Data sources and sampling sites

The water quality monitoring data are from the Wenzhou Environmental Monitoring Center and Pingyang Environmental Monitoring Stations (Zhang and Zhang, 2006). The economic data for agriculture, industry, and populations are based on the Wenzhou Statistics Bureau (2001). The wastewater release was calculated using the method of coefficients, which is based on the integration of empirical release coefficients per unit product from multiple years and locations to estimate the amounts of pollutants released.

The formula is defined as $W = K*A*B*C + D$, where W refers to wastewater release in 10,000 ton; K refers to the number of enterprises; A refers to product wastewater discharge in 10,000 ton per ton of product and number of processing machines; B refers to number of processing machines per enterprise; C refers to tons of product produced per unit of processing machine; and D is the other water use in 10,000 ton.

The sampling sites were in Litou, Jiangyu, Fangyanxia, and Jiangkou for the Aojiang watershed (Fig. 1), and in Xiao Dan, Yang Fu Shang, Longwan for the Oujiang watershed. The sampling periods were from 1992 to 2003. Samples were taken two times during 'Ping Shui Qi' (the dry period receiving around 25% of the annual rainfall): March–May, October, and November; then two times during "Feng Shui Qi" (the wet period receiving close to

Fig. 1. Locations of the study area, Wenzhou metropolitan area including the Oujiang river and Aojiang river watersheds, and the water quality sampling sites indicated as the star symbols.

Table 1
Standards of environmental quality for surface water (National EPA, 2001)

Quality types	Chem. oxygen demand <=	Sediments <=	Biochem. oxygen demand <=	Ammonium nitrogen <=	Total germanium <=
Type I	<15	—	<3	0.02	0.01
Type II	15	—	3	0.02	0.05
Type III	20	—	4	0.02	0.05
Type IV	30	—	6	0.2	0.05
Type V	40	—	10.00	0.20	0.10

"<=" refers to the value less than or equal to.

60% of the annual rainfall): June–September; and two times during 'Ku Shui Qi' (the very dry period receiving about 15% of the annual rainfall): December–February. The annual concentrations were the averages of these samples.

2.3. Analytical methods and standards for the evaluations

The chemical reaction involved in the leather industry uses Na_2CrO_4 to change Ge to Ge^{3+}, which is discharged with wastewater along with another side product, NH_4^+-N. The analytical methods of GB/T7479—1987 (National EPA, 2001) and GB/T7467—1987 (National EPA, 2001) were used to analyze the concentrations of NH_4^+-N and Ge. The unit for measuring the contaminant concentrations was 'mg/L' and the unit for measuring the loadings was 'ton'. The monitoring samples were analyzed by Wenzhou Environmental Monitoring Center and Pingyang Environmental Monitoring Station.

Water quality was evaluated using the standards of GB3838-2002 (Table 1) and wastewater was evaluated using the standards of GB8979-1996 (Table 2).

Ammonium nitrogen and total germanium are the focus of the study. In addition, the amount of chemical oxygen demand (COD), biochemical oxygen demand (BOD), and sedimentation in the wastewater was also examined.

Table 2
Standard values of releasing water containing pollutants (National EPA, 2001)

Release quality types	Chem. oxygen demand < =	Sediments < =	Biochem oxygen demand < =	Ammonium nitrogen < =	Total germanium < =
First class	<15	—	<3	0.02	0.01
Second class	15	—	3	0.02	0.05
Third class	20	—	4.00	0.02	0.05

"< = " refers to the value less than or equal to.

An integrated pollution index and standard exceeding index were used in this study to evaluate the water quality. The integrated pollution index is defined as the summation of the ratio of the annual average concentration of each pollutant to its standard concentration. The formula is as follows:

$$P_j = \sum_{i=1}^{n} P_{ij}, \quad k_i = \frac{p_{ij}}{pj} \times 100\%, \quad p_{ij} = \frac{c_{ij}}{c_{io}}, \tag{1}$$

where P_j refers to the water quality integrated pollutant index in the jth profile, P_{ij} refers to the ith pollutant integrated pollution index in the jth profile, C_{ij} is the annual average of the ith pollutant in the jth profile, C_{io} is the annual average of the ith pollutant, k_i refers to the coefficient of the ith pollutant in the jth profile, and n is the number of pollutants in the evaluation.

The exceeding index is defined as the ratio of the ith pollutant to its standard. The formula is as follows:

$$T_i = \frac{B_{il}}{B_{io}}, \tag{2}$$

where T_i refers to the exceeding index of the ith pollutant, B_{il} refers to the lth monitoring result for the ith pollutant, and B_{io} refers to the evaluation standard for the ith pollutant.

Statistical regression and correlation methods were used in this study to assess the relationships of water quality and released wastewater and other factors. The linear regression model is described as

$$Y = a + bX, \tag{3}$$

where b-regression coefficient

$$b = \frac{\Sigma(x-\bar{x})(y-\bar{y})}{\Sigma(x-\bar{x})^2}, \tag{4}$$

a-regression intercept

$$a = \frac{1}{n}\sum y - b\frac{\Sigma x}{n} = \bar{y} - b\bar{x}. \tag{5}$$

Y refers to the concentrations of the pollutants, while X refers to the amount of released wastewater.

Correlation coefficient:

$$r = \frac{S_{xy}}{\sqrt{S_{XX}S_{yy}}}, \quad S_{xx} = \sum_{i=1}^{n}(x_i-\bar{x})^2, \tag{6}$$

$$S_{XY} = \sum_{i=1}^{n}(x_i-\bar{x})(y_i-\bar{y}). \tag{7}$$

3. Results

3.1. Changing patterns of the NH_4^+-N, total Ge and released wastewater

The amount of NH_4^+-N increased with a slope of 651.6 tons/year and $r^2 = 0.94$ during the period of 1992–1998 in the Aojiang watershed, as indicated by the data from Pingyang county (Fig. 2). The maximum amount of NH_4^+-N in 1998 reached 3952 tons. After 1998, the amount of NH_4^+-N in the released water started to decrease with a slope of −326.6 ton/year and $r^2 = 0.76$. In 2003, the amount of NH_4^+-N decreased to 2069 tons, a 47.6% decrease from 1998. In the Oujiang watershed, the NH_4^+-N amount in Lucheng increased from 412 tons in 1992–3095 tons in 1999, an increase of 651%. After 1999, the amount of NH_4^+-N decreased to 1810 tons in 2003, a decrease of 41.5%. In Ouhai of the Oujiang watershed, the amount of NH_4^+-N increased from 1355 tons in 1994 to 2186 tons in 1997, an increase of 61%. After 1997, the amount of NH_4^+-N decreased to 416 tons in 2003, resulting in an average decrease of 80% (Fig. 2).

The total germanium increased with a slope of 15.54 tons/year and $r^2 = 0.92$ in the Aojiang watershed, as indicated by the data from Pingyang during the time period of 1992–1998 (Fig. 3). The maximum amount of total germanium was 91.9 tons in 1998. From 1998 to 2003, the amount of total germanium decreased with a slope of −8.98 tons/year and $r^2 = 0.81$. In 2003, the amount decreased to 45.7 tons, a 50.2% decrease from 1998. In Lucheng of the Oujiang watershed, the total germanium increased from 8.8 tons in 1992 to 80 tons in 1998 (Fig. 3). After 1998, the amount of germanium decreased, and the amount was 42.2 tons in 2003, an average decrease of 47.3%. In Ouhai of the Oujiang watershed, the amount of germanium increased from 6.6 tons in 1992 to 41 tons in 1997. The amount of Ge was 20 tons in 1998 and then decreased to 12.75 tons in 2003, an average decrease of 69% (Fig. 3). These relationships are statistically significant at the significance level of 0.01.

Fig. 4 shows the trends of released wastewater in the leather industry for Pingyang, Lucheng, and Ouhai in the

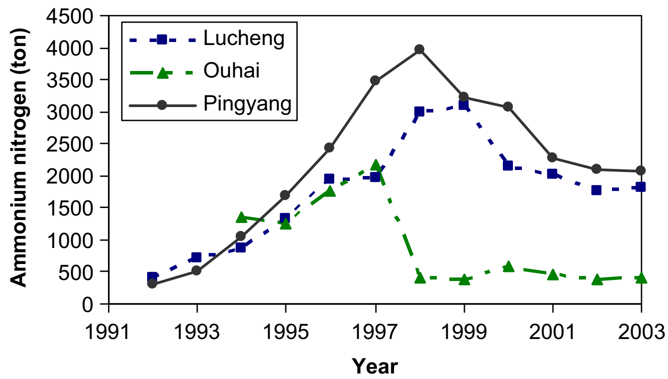

Fig. 2. The releasing trend of ammonia nitrogen in wastewater from 1992 to 2003.

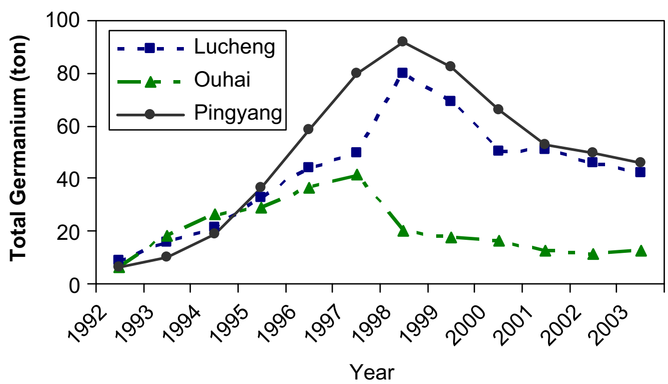

Fig. 3. The releasing trend of total germanium in wastewater from 1992 to 2003.

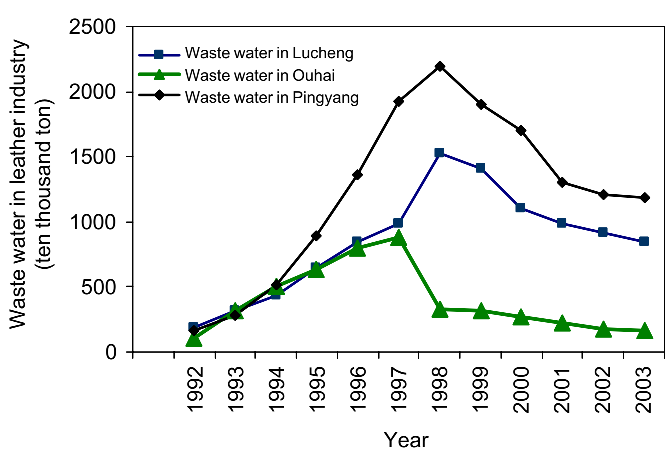

Fig. 4. The trend of annual wastewater released from leather industry in Pingyang, Lucheng and Ouhai from 1992 to 2003.

Wenzhou metropolitan area. Pingyang released more wastewater than Lucheng and Ouhai. The peak of wastewater release was 22 million tons in 1998 for Pingyang and 15.2 million tons for Lucheng while the peak release for Ouhai was 8.8 million tons in 1997 (Fig. 4).

The relationship of ammonium nitrogen and germanium with released wastewater from both the Aojiang and Oujiang watersheds is shown in Fig. 5. It is clear that the relationship between the ammonium and released wastewater is linear, similar to the correlation between germanium and wastewater. Using annual pollutant loading and released wastewater data, the amount of NH_4^+-N increased as wastewater release increased according to Y_1 (ton) $= 128.82 + 1.78X_1$ (10,000), where Y_1 is the amount of NH_4^+-N, and X_1 is the amount of released wastewater from the leather industry. The determination coefficient of this regression is 0.941 ($p < 0.01$) and is statistically significant, meaning that more than 94% of the ammonium nitrogen was from the released wastewater from the leather industry in the Aojiang and Oujiang watersheds in the Wenzhou metropolitan area. The regression equation also indicates that an increased release of ten thousand tons of water would be associated with an increased amount of NH_4^+-N of 1.78 tons.

When the data were analyzed separately for Pingyang, Lucheng and Ouhai, the relationship between NH_4^+-N and released wastewater was similar to the relationship based on aggregated data for the three places. In the Aojiang watershed, based on the Pingyang data, Y_{11} (ton) $= 53.35 + 1.74X_{11}$ (10,000 tons), where Y_{11} is the amount of NH_4^+-N, and X_{11} is the amount of released wastewater from the leather industry in Pingyang. The determination coefficient of this regression is 0.996 ($p < 0.01$), meaning that more than 99% of the ammonium nitrogen was from the released wastewater from the leather industry in this region. In the Oujiang watershed, based on the Lucheng data, Y_{12} (ton) $= 33.93 + 2X_{12}$ (10,000 tons), with a determination coefficient of 0.96 ($p < 0.01$), signifying that more than 96% of the ammonium nitrogen was from the released wastewater from Lucheng's leather industry. In the Oujiang watershed, based on the Ouhai data, Y_{13} (ton) $= -150.18 + 2.48X_{13}$ (10,000 tons), with a determination coefficient of 0.86 ($p < 0.01$), showing that more than 86% of the ammonium nitrogen was from the released wastewater from the leather industry in Ouhai.

Similarly, the total germanium increased as the released wastewater increased. Y_2 (ton) $= 3.76 + 0.041X_2$ (10,000 tons), where Y_2 is the amount of total germanium and X_2 is the amount of released wastewater from the leather industry, based on aggregated data from the three places, Pingyang, Lucheng and Ouhai. This relationship indicated that total germanium is linearly associated with the released wastewater (Fig. 5). The determination coefficient for this regression is 0.93 ($p < 0.01$) and is statistically significant. When the released wastewater increased by 10,000 tons, the total germanium increased by 0.041 tons.

When the data were analyzed separately for Pingyang, Lucheng and Ouhai, the relationship between Ge and released wastewater was similar to the relationship based on aggregated data for the three places. In the Aojiang watershed, based on the Pingyang data, Y_{21} (ton) $= -1.95 + 0.0425X_{21}$ (10,000 tons). The determination coefficient for this regression is 0.994 ($p < 0.01$) and statistically significant. In the Oujiang watershed, based on the Lucheng data, Y_{22} (ton) $= -0.91 + 0.05X_{22}$ (10,000

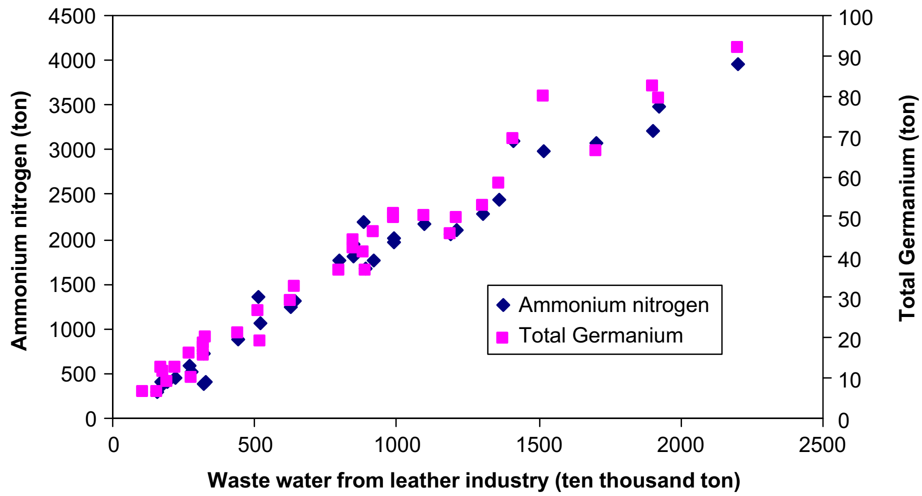

Fig. 5. The relationship between the released wastewater and ammonia nitrogen and total germanium in the Oujiang and Aojiang watersheds.

tons), with a determination coefficient of 0.98 ($p<0.01$), meaning that more than 98% of the total germanium was from the released wastewater in leather industry in Lucheng. In the Oujiang watershed, based on the Ouhai, Y_{23} (ton) $= 5.08+0.04X_{23}$ (10,000 tons), with a determination coefficient of 0.98 ($p<0.01$), signifying that more than 98% of the total germanium was from the released wastewater from the leather industry in Ouhai.

For both contaminants, the slopes of the three regression equations developed from separate data from Pingyang, Lucheng and Ouhai did not show any statistical difference. Therefore, it is statistically appropriate to use aggregated equations for each contaminant to estimate the total Ge and ammonium nitrate associated with the released wastewater for management decisions.

3.2. Wastewater and integrated pollution index

Fig. 6 shows the changing trend of the integrated pollution index in the two watersheds. In the Aojiang watershed, the pollution index increased to a value of 102 in 1999, an increase of 72% when compared to the value in 1992. From 1999 to 2000, the value decreased to a value of 81, a 21% decrease. However, in the Oujiang watershed, the pollution index increased to a value of 1.58 in 1995, an increase of 48% when compared to a value in 1992 (Fig. 6). After 1995, the index decreased to the value of 0.485 in 2000, a decrease of 69.3%.

Fig. 7 shows the relationship between the integrated pollution index and the released wastewater from the leather industry. As the released wastewater increases, the integrated pollution index also increases; there exists a linear relationship between wastewater and the integrated pollution index. Thus for the Aojiang wateshed, $P_j = -13+0.0482W$, where P_j is the integrated pollution index, and W is the released wastewater from the leather industry (10,000 tons). This relationship is statistically significant at $p<0.01$, with a determination coefficient of

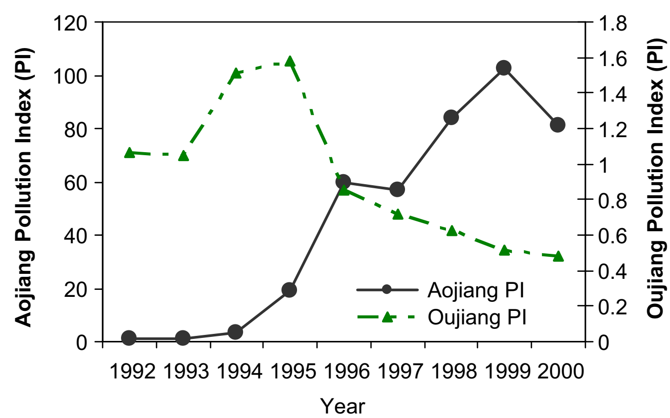

Fig. 6. The changing trend of the integrated pollution index of Aojiang and Oujiang watersheds from 1992 to 2000.

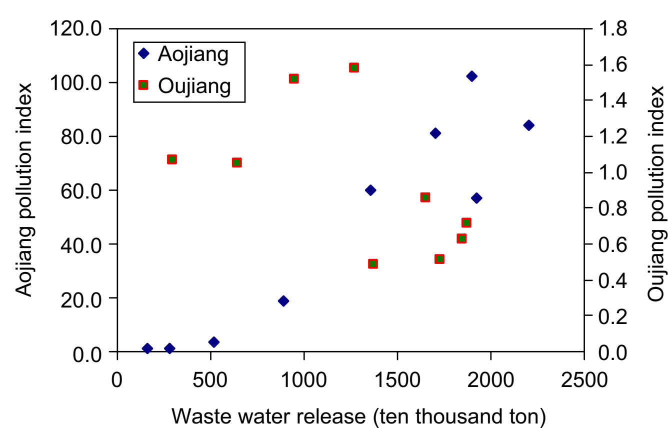

Fig. 7. The relationship between the wastewater released from leather industry and the integrated pollution index in Aojiang and Oujiang watersheds.

0.86, indicating that 86% of the pollution was from the wastewater. The linear relationship also illustrates that an increase of 10,000 tons of wastewater release will raise the

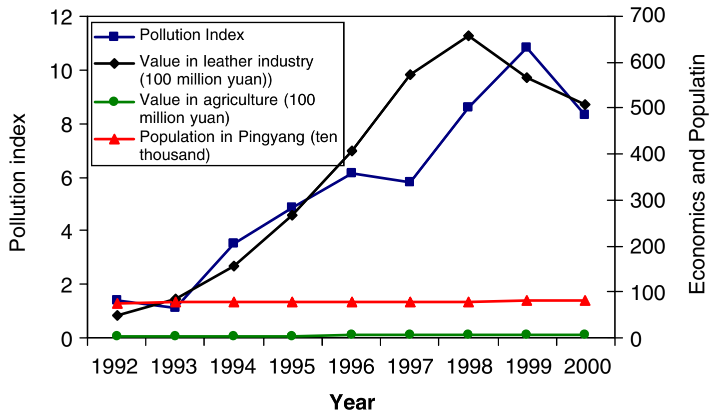

Fig. 8. The relationship between the integrated pollution index and the economics and population growth in Pingyang county from 1992 to 2000.

integrated pollution index to a value of 0.0482. However, the relationship of the integrated pollution index and the released wastewater is different in the Oujiang watershed when compared to the Aojiang watershed. The integrated pollution index in the Oujiang watershed increased with increased wastewater release before 1995, but then decreased with increased wastewater release after 1995. The reverse relationship was observed at the value of 14 million tons wastewater (Fig. 7) in the Oujiang watershed. Using a simple linear regression model, the integrated pollution index for the Oujiang watershed is $Pj = 1.43–0.00039W$, where Pj is the integrated pollution index, and W is the released wastewater (10,000 tons). The determination coefficient is 0.28. It is obvious that the relationship is positive and strong for the Aojiang watershed, and negative and weak for the Oujiang watershed.

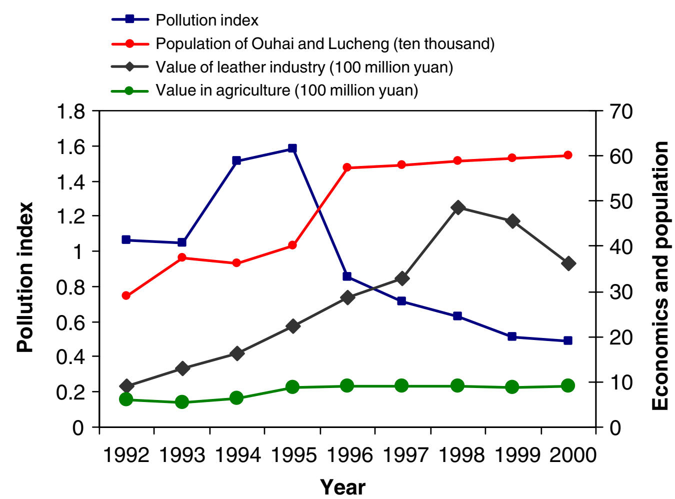

Fig. 9. The relationship between the integrated pollution index and the economics and population growth in Ouhai and Lucheng districts from 1992 to 2000.

3.3. Evaluations of integrated pollution index, water quality, and economics

To further understand the integrated pollution index, Figs. 8 and 9 show the relationship of the pollution and the economics of agriculture and industry in the counties where the watersheds are located. In the Aojiang watershed, during the period from 1992 to 2000, the population and the agricultural economics increased slightly, and the industrial economy dramatically increased. However, the integrated pollution index increased from 1992 to 1996 by 4175%, decreased in 1997 by about 5%, and then increased again in 1998 and 1999. After 1999, the integrated pollution index decreased 21% (Fig. 8). In the Oujiang watershed, pollution increased until 1996 and has since stabilized, while agriculture did not change much during the 1992–2000 period. However, the leather industry economy steadily increased until 1998, and then declined. The integrated pollution index in the Oujiang watershed showed an increase in 1994 and then a decrease after 1995–2000 (Fig. 9).

Table 3 shows the average exceeding index, its standard deviations, and the coefficient of variations for the contaminants studied in the paper. These measures were used to further evaluate the water quality in the watersheds. In the Aojiang watershed, the COD exceeded the standard 22 times, sedimentation over 43 times, BOD 57 times, NH_4^+-N 12 times, and Ge 3 times (Table 3). Their associated standard deviations were rather small. This may mean that the magnitude of each pollutant was consistently high throughout the time period. Their associated coefficients of variation were as follows: 9.7% for COD, 3.5% for sediments, 5.6% for BOD, 4.9% for NH_4^+-N, and 6.2% for Ge, respectively (Table 3). In Lucheng of the Oujiang watershed, the COD exceeded the standard 22 times, sedimentation over 45.3 times, BOD 53.7 times, NH_4^+-N 13.9 times, and Ge 3.3 times (Table 3). Their associated standard deviations were also small, with associated coefficients of variation as follows: 7.1% for COD, 8.4% for sediments, 15.1% for BOD, 5.9% for NH_4^+-N, and 4.3% for Ge, respectively (Table 3). In Ouhai of the Oujiang watershed, the COD exceeded the standard 22 times, sedimentation over 35.4 times, BOD 47.5 times,

Table 3
Comparisons of environmental quality parameters in the three selected study areas (1992–2000)

	Chem. oxygen demand	Sediments	Biochem. oxygen demand	Ammonium nitrogen	Total germanium
Lucheng					
Average	21.76	45.25	53.71	13.86	3.31
Standard deviation	1.54	3.80	8.11	0.82	0.14
Coeff. of variation, %	7.07	8.39	15.10	5.89	4.27
Ouhai					
Average	21.83	35.42	47.51	13.74	3.78
Standard deviation	1.26	2.67	4.26	3.22	0.56
Coeff. of variation, %	5.77	7.52	8.96	23.46	14.78
Pingyang					
Average	22.00	43.24	56.57	12.09	2.68
Standard deviation	2.13	1.51	3.18	0.59	0.16
Coeff. of variation, %	9.67	3.50	5.62	4.89	6.16

"$<=$" refers to the value less than or equal to.

NH_4^+-N 13.7 times, and Ge 3.8 times (Table 3). Their associated standard deviations were also small and their associated coefficients of variation were as follows: 5.8% for COD, 7.5% for sediments, 9.0% for BOD, 23.5% for NH_4^+-N, and 14.8% for Ge, respectively (Table 3).

From the above results, one can see that the most severe pollution was related to the BOD. When the constituents are compared among the three locations, we found that the average sediments exceeding the standards in Ouhai are significantly lower ($p<0.01$) than those in Lucheng and Pingyang (Table 3). However, the other constituents do not demonstrate statistical difference between the three locations. Moreover, the standard deviations of NH_4^+-N and Ge in Ouhai are significantly higher ($p<0.01$) than the standard deviations in the other two places. Among all constituents tested in the study, the most harmful pollutants to human and aquatic species are NH_4^+-N and Ge.

In the last decade, using the standard of each constituent in Table 1 (National EPA 2001) for determining water quality, the Aojiang watershed water quality dropped to Type IV or V in 2003 from Type III in 1992. In 1997, one of the four locations sampled for the monitoring still remained at Type III. This indicated that the water quality dramatically degraded in the last 10 years in the Aojiang watershed. When compared to the Aojiang watershed, water quality in the Oujiang watershed declined to Type III in 1995 from Type II in 1992. However, the water quality in the Oujiang watershed became Type II in 1997 and 1998, then changed to Type IV in 1999 and Type III in 2000. Although water quality in the Aojiang watershed steadily declined, water quality in the Oujiang watershed fluctuated and also degraded to a point requiring attention. These two watersheds contained similar leather industries as the local main enterprises. However, the integrated pollution index in the Oujiang watershed decreased since 1996 (Fig. 7), and the integrated pollution index in the Oujiang watershed was negatively correlated with the released wastewater.

4. Discussion and conclusions

4.1. Influence of policy and ecosystem impacts

The simultaneous occurrence of the decreasing trend in the integrated pollution index and the increasing trend towards an industrial economy after 1999 indicated that the pollutants associated with the leather industry could be reduced by using more advanced technologies and proper industry management, as well as implementing government regulations. Sine 1996, the Chinese National Environmental Protection Agency (EPA) has implemented policies regulating surface water quality (National EPA, 1997). These policy reinforcements have confirmed that controlling the production from extremely small-sized, poorly managed processing enterprises could effectively reduce the wastewater release from the leather industry. This may be one of the reasons why the loads of ammonium nitrogen and total germanium were reduced after 1998. Industries strictly following the guidelines of materials processing can also help reduce pollution. In addition, the proper investment in water treatment plants can effectively reduce the pollutants in released wastewater. It is very clear that controlling the wastewater release into the major rivers can improve the water quality in the Aojiang and Oujiang watersheds. It is especially important to control the release of NH_4^+-N and Ge from the areas where heavy leather industry is concentrated.

It is well documented in the literature that the impact of high nitrate concentrations in drinking water cause blue baby syndrome and high nitrate concentrations in the river systems cause river eutrophication (Skipton and Hay, 1998, Bianchi et al., 1999; Cébron et al., 2003, Radwan et al., 2003). High concentrations of nitrogen can also reduce the blood oxygen transfer and destroy respiratory system tissues, which leads to death due to an inability to exchange oxygen and waste gas (Cooke and Kalita, 2002; Hubei Keliang Company, 2003) in fish species. As for the Ge toxicity, Wang and Ding (2002) reported that Ge3+ can fix proteins and can harm human health as well as harm fish species (Lide, 1998; Gao and Su, 2001; Lenntech, 2004).

Although it is difficult to quantify the impact of ammonium nitrogen and germanium pollutants from the released wastewater on human and ecosystem health, the potential long-term effects of these pollutants are foreseeable. Xie (2004) and Liu (2005) pointed out that, in this region, the crops had little harvest, the air had a bad odor, strange diseases frequently prevailed, the streams and rivers contained blackish film floating on the water, and human health was severely impacted. This heavy impact of the pollutants forced many families to move out of the region in the Aojiang watershed (Xie, 2004; Liu, 2005). Although the Oujiang watershed water quality is not as criticized at present, the public's impression is that the degraded water quality has caused many unknown diseases in the Lucheng and Ouhai regions.

Historically, people in the Aojiang amd Oujiang watersheds, especially downstream, rely on fishing for a living. Because of the advancement of science and technology, the tidal aquaculture activities and farm size near the bay area have increased in recent years. In 2003, aquaculture farm size reached close to 1500 ha in Longgang town, and close to 70 ha in Aojiang town (Wenzhou Ocean and Sea Bureau, 2003). More than 2307 ha of aquaculture farms were distributed in the Oujiang watershed, according to Wenzhou statistics. The types of fisheries in these two watersheds included crabs, shrimps, clams, and some fish types. These species require the water standard to be Type III or better, following GB3838-2002 (National EPA, 2001). If the water quality is lower than Type III, the ecosystem health will be degraded and thus, the species numbers will automatically be reduced. Therefore, this degraded ecosystem and water quality will impact fishery economic development, which will then influence the living standard in the region. In addition, bioaccumulation of heavy metals in fisheries is also a possibility which will affect food safety. Research on sediments and toxicity of these contaminants will be important to further understand the severe impacts.

Using the estimation developed in this study, the annual wastewater in the Aojiang watershed should be limited to less than 2.9 million tons, which would be one-fourth of the current wastewater release. The annual wastewater release in the Oujiang watershed should be regulated to less than 11 million tons. If this goal can be achieved, then the water in the watersheds can be maintained at the First class (Table 2) of the wastewater release standard, and the Type III or II surface water quality standard (Table 1). In the same way, if the annual release of NH_4^+-N can be reduced to less than 43.5 tons, and total germanium annual release limited to less than 4.35 tons for the Aojiang watershed, the wastewater from the leather industry in the Aojiang watershed will meet the wastewater release standards, GB8979-1996 (National EPA, 2001) at the First class (Table 2). Assuming other conditions remain the same, if the annual release of NH_4^+-N in the Oujiang watershed can be restricted to less than 165 tons, and total germanium annual release can be controlled at less than 16.5 tons, the wastewater from the leather industry in the Oujiang watershed will meet the wastewater release standards, GB8979-1996 (National EPA, 2001), at the First class (Table 2) as well and surface water quality will meet GB3838-2002 standards at Type II and III levels.

For improving the water quality in the watersheds, it is critical and important to understand the need for education in environmental protection, and understand the relationship between environmental quality and economic development (China Net, 2005). Balancing this relationship can help local and state governments to foresee the short-term and long-term benefits (Fenech et al., 2003) of sustainable economic development and environmental pollution controls. The deteriorating environment can affect the sustainable development of the economy in the region. Therefore, government agencies should work together with local organizations to address the environmental quality issues in the watersheds. Also, the industries need to adopt advanced technological solutions, as well as improve practical methods and management, so as to adjust for these important environmental quality concerns.

4.2. *Effective contamination control methods and strategies*

The analyses and the results from this study illustrated that the development of the leather industries in the Aojiang and Oujiang watersheds was associated with severe pollution impacts on human health and the degradation of the environment. Conventional economic impact models often lack the environmental linkages necessary for examining the connections between environmental stewardship and economic sustainability (Fenech et al., 2003; Hansell et al., 2003). A healthy environment results when there is harmony between human concerns and ecosystem needs. Such an environment leads to higher overall productivity without sacrificing long run sustainability.

National and international contamination control experiences (Xia et al., 2003; Kong et al., 2003; Oke, 2004) revealed that it is important to integrate contamination control with source prevention, and scientific research with technological management and government policies. Source control through the promotion of technology advancement in industry such as wastewater treatment plants, changes in material inputs, and adjustment of manufacture product structures can be considered effective. Moreover, adopting new technology, processes, and equipment, initiating sanitary programs in production lines, and reducing release of pollutants are all excellent methods to achieve both economic and environmental benefits. To improve water quality, it has been reported in the literature that artificial wetlands can play an important role in purifying water (Xia et al., 2003; Karczmarczyk, 2004). These methods can be effective in removing up to 50% of pollutants. In addition, research also showed that some plant species could effectively remove high concentrations of harmful materials (Xia et al., 2003; Kong et al., 2003) and hence, reduce the concentrations of detrimental materials. From the chemical viewpoint, NH_4^+ can be oxidized to NO_3^- to reduce the amount of NH_4^+ in water. However, the chemical method for removal of total Ge does not work as well. Combining technological, chemical, and biological removal of the contaminants, a healthier environment as well as economic development can be sustained.

4.3. Conclusions

To summarize, we found that the ammonium nitrogen and total germanium increased from 1992 to 2003, while the wastewater releases also increased during this period. The integrated pollution index indicated that pollution increased linearly with released wastewater in the Aojiang watershed, but the relationship fluctuated in the Oujiang watershed. Results also indicated that increased economic activity did not have to be associated with degraded water quality (in this case, increased wastewater release from the leather industry at the regional level).

Through the discussion of the findings in the paper, it is clear that controlling and/or reducing the contamination in Wenzhou can be achieved through source control and mitigation. We also suggest increasing the level of environmental regulations and policies, building water treating plants, and strengthening private and public capital resources for wastewater treatment and management.

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