

Article

# Risk Assessment of Nitrogen and Phosphorus Loss in a Hilly-Plain Watershed Based on the Different Hydrological Period: A Case Study in Tiaoxi Watershed

Hongmeng Ye <sup>1,2</sup>, Xuyin Yuan <sup>1,2,\*</sup>, Lei Han <sup>2</sup>, Ja Bawk Marip <sup>2</sup> and Jing Qin <sup>3</sup>

<sup>1</sup> Fujian Provincial Key Laboratory of Eco-Industrial Green Technology, College of Ecology and Resource Engineering, Wuyi University, Wuyishan 354300, China; hongmengye@sina.com

<sup>2</sup> Key Laboratory of Integrated Regulation and Resources Development of Shallow Lakes of Ministry of Education, College of Environment, Hohai University, Nanjing 210098, China; hanlei8613@163.com (L.H.); maripjabawk@gmail.com (J.B.M.)

<sup>3</sup> China Institute of Water Resource and Hydropower Research, Beijing 100038, China; qinjing@iwhr.com

\* Correspondence: xxy\_hjy@hhu.edu.cn; Tel.: +86-025-8378-6697

Received: 1 July 2017; Accepted: 17 August 2017; Published: 22 August 2017

**Abstract:** Non-point source pollution is widely considered a serious threat to drinking water. Eutrophication in Chinese watershed is mainly due to nitrogen and phosphorus output from agricultural source. Taihu Lake is a typical eutrophic lake in China, a basin representative for the study of the temporal-spatial characteristics of pollution loading of nitrogen and phosphorus to provide scientific basis for reasonable estimation and targeted control measures of nitrogen and phosphorus loss. Based on data from nitrogen and phosphorus loss in agricultural land, livestock breeding, domestic discharge and aquaculture, this study calculated the levels of nitrogen and phosphorus comprehensive loss risk for each pollution source. Using the superposition of ArcGIS raster data, we also described the spatial distribution of nitrogen and phosphorus comprehensive loss risk by the formula of comprehensive loss risk. The results showed that critical risk areas of nitrogen and phosphorus loss mainly originated from livestock breeding and agricultural land during flood period in Tiaoxi watershed. Agricultural land and livestock breeding sources formed major parts of nitrogen loss, accounting for 30.85% and 36.18%, respectively, while phosphorus loss mainly originated from livestock breeding (56.28%). During non-flood period, integrated management of livestock breeding and domestic discharge requires much attention to control nitrogen and phosphorus loss in the critical risk area. Finally, it is of great practical significance to propose spatial-temporal targeted measurements to control nitrogen and phosphorus pollution in watershed for various periods and different areas.

**Keywords:** non-point source pollution; flood season; non-flood period; nitrogen and phosphorus loss; risk assessment; critical risk area; watershed

## 1. Introduction

Non-point source pollution has been considered one of the greatest threats to drinking water [1,2], and has received increasing attention in recent decades [3]. Load calculation of non-point source pollution is much more difficult than point source pollution, due to challenges such as the breadth, randomness, uncertainty and difficulty in monitoring [4]. In China, the key issue of water pollution is the eutrophication caused by non-point source pollution [5]. According to the first national pollution census bulletin, nitrogen and phosphorus outputs from Chinese agricultural source in watershed accounts for 57.19% and 67.27% of total nitrogen and total phosphorus pollution sources,

respectively [6]. Generally, nitrogen and phosphorus agricultural non-point sources including agricultural land, domestic discharge, livestock breeding and aquaculture [1,5], contribute much more to eutrophication than point source pollution from urban areas and industrial enterprises [4].

Nitrogen and phosphorus loss index system method is a semi-quantitative evaluation indicator system based on the source of agricultural non-point source pollution factor and migration factor, using simple mathematics to assess the risk level of nitrogen and phosphorus loss from various pollution sources to water [7,8]. Different from traditional quantitative assessment of physical model, this indicator system method is advantageous. It has lower data demand, convenient operation, short running cycle, and better performance; provides spatial distribution of nitrogen and phosphorus loss in watershed; and distinguishes the critical risk areas, accounting for effective restoration measures [9,10].

Thus far, the indicator system is applied to spatial differentiation of non-point source pollution of nitrogen and phosphorus rather than temporal variability. In fact, the loss process of nitrogen and phosphorus is a complicated process, with respect to spatio-temporal variability, due to climate, topography, soil, rainfall, land use and farmland management and other factors [11]. For instance, nitrogen and phosphorus contents in agricultural land can be affected by differential fertilization in different seasons [12]; nutrient content of domestic sewage and household garbage will also be changed by seasonal effects of resident lifestyle [13–15]; and the release of breeding waste (dung and urine) can be influenced by different livestock breeding activities of seasonal alternation [16,17]. Therefore, the nitrogen and phosphorus loadings from different pollution sources could have different seasonal discharge patterns, and different types of non-point sources may show various contribution degrees. In addition, the changes in influencing factors such as climate, rainfall and runoff, corresponding to different seasons, will further disturb the migration and transformation process of nitrogen and phosphorus in watershed. Particularly, rainfall intensity largely impinges on the amount of runoff yield, surface runoff, soil erosion and nutrient output [18–20]. Therefore, it is conducive to distinguish temporal heterogeneity of nitrogen and phosphorus derived factors and migration factors, estimate the spatial distribution of non-point sources in flood and non-flood seasons, screen out critical risk areas, and analyze contributions of different pollution source to take effective measures for targeted nitrogen and phosphorus control in watershed.

Tiaoxi watershed is a main water source and has significant impact on water quality of Taihu, which shows a typical eutrophic status in nearshore areas [20]. Tiaoxi watershed is an agricultural economic developed area, with hilly area in the upstream and river network plain in the middle and lower reaches. There is a flood period from April to September every year, and rainfall accounts for more than 75% of annual precipitation. Other months are non-flood seasons, with rainfall accounting for less than 25% of annual precipitation [21]. Therefore, it is very representative to choose this catchment area for the study of temporal-spatial characteristics of non-point source pollution load of nitrogen and phosphorus since this can provide scientific basis for reasonable estimation and risk control of nitrogen and phosphorus loss in the watershed.

The aims of this study are: (1) to analyze the different risk levels of nitrogen and phosphorus loss from different non-point sources in Tiaoxi watershed; (2) to apply index system method to estimate temporal-spatial distribution characteristics of nitrogen, phosphorus and comprehensive pollution risks in Tiaoxi watershed; and (3) to find the critical risk areas and their contribution during different periods; all in effort to put forward the pertinence of the comprehensive measures of nitrogen and phosphorus pollution prevention in this watershed.

## 2. Region and Methods

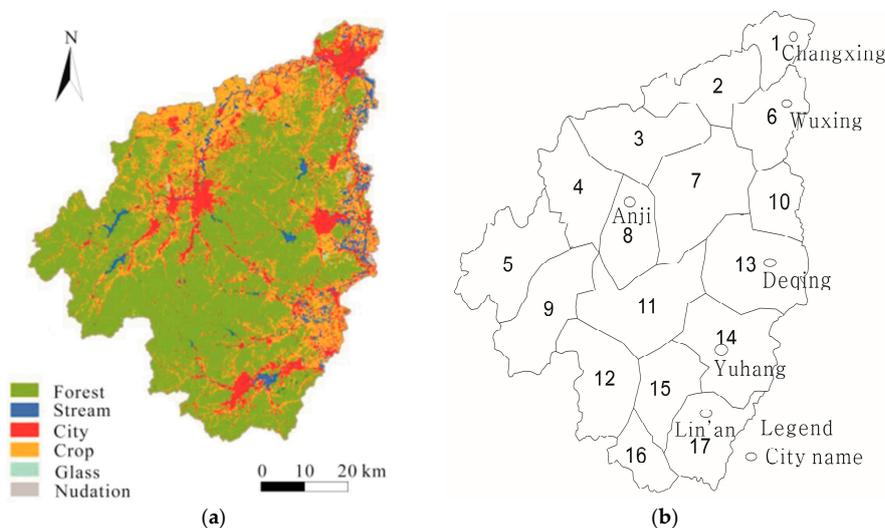
### 2.1. Description of the Study Area

Tiaoxi watershed, belonging to Taihu water system of Yangtze River Basin, is located in northwest of Zhejiang Province (30°07'~30°41' N, 119°07'~119°08' E), with a length of 157.4 km and a drainage

area of 4576.4 km<sup>2</sup>. East Tiaoxi and West Tiaoxi are two major tributaries. The upper reaches of the Tiaoxi River flow through the low-hill region of western Zhejiang Province, and shows mountainous river features and land use types of bamboo and tea forest. The middle and lower reaches flow through plain landform, which features the plain river and land use type of paddy field, vegetable farmland and weeds. In Tiaoxi watershed, the annual average temperature is 15.5–15.8 °C and the average annual precipitation is 1460 mm, with the unbalanced temporal distribution for more than 75% of annual precipitation from April to September and less precipitation in non-flood period from October to March [21].

Tiaoxi watershed has seven provincial-level economic development zones and extends across six county-level cities including Lin'an and Yuhang cities in Hangzhou metropolis and Deqing, Anji, Wuxing and Changxing cities in Huzhou metropolis. According to the statistical yearbook of each city in 2010–2011, this watershed has a population of 2.3 million and a population density of 403 people per square kilometer, which is a relatively developed region in Zhejiang Province, with regards to income of 54,292 RMB per capita. In recent years, with the rapid development of the social economy, the urbanization process of this rural area has further expanded, hence, contributing to the increase of livestock and aquaculture breeding within Tiaoxi watershed. Moreover, the problem of agricultural non-point source pollution has become more prominent, seriously affecting water quality and causing eutrophication of watercourse, which threatens the water-supply security and sustainable development of Tiaoxi watershed.

Figure 1 shows the water system distribution of Tiaoxi watershed and sub-watershed divisions of study area, using the function of water system generation and watershed segmentation by SWAT model (Soil and Water Assessment Tool). We then extracted the landform from digital elevation model (DEM). Generated water system diagram was adjusted and supplemented by referring to rivers with land use types (Figure 1a) to ensure the accuracy of water system division. The study area was divided into 17 sub-watershed based on the above-mentioned regulations (Figure 1b).



**Figure 1.** Land use types (a) and sub-watershed divisions (b) in Tiaoxi watershed.

## 2.2. Nitrogen and Phosphorus Loss Index

Nitrogen and phosphorus loss system is a semi-quantitative evaluation method, which considers factors affecting nitrogen and phosphorus pollution in agricultural non-point source comprehensively, and evaluates nitrogen and phosphorus loss risk magnitude of different areas within watershed [10,22]. Model indexes are divided into two categories: source factors and migration factors. Source factors of nitrogen and phosphorus are the same, and the migration factors are different. The migration factors of nitrogen are mainly soil texture and soil permeability while surface runoff and soil erosion are the main

migration factors for phosphorus [22]. Therefore, the confirmation of nitrogen and phosphorus source factors should be based on the realities of study area and suitable migration factors when using this index model, and then the corresponding weights should be endowed according to the contribution to nitrogen and phosphorus loss of each impact factor. The source factors and migration factors will be divided into several levels to calculate the nitrogen and phosphorus risk index according to corresponding grade values and specific rules [11,23]. The value of weight is decided by local nitrogen and phosphorus loss and references to relevant reports and expert suggestions.

### 2.2.1. Calculation of Source Factors

Source factor system was mainly applied for the evaluation of nitrogen and phosphorus discharge intensity in each pollution source. Based on the categories of agricultural non-point source in watershed and loss characteristics, the primary non-point source in this watershed was mixing source, and the source factors of nitrogen and phosphorus discharge included agricultural land (including forest land), livestock breeding, aquaculture and domestic discharge [5,24]. In this study, calculation of source factors in flood period (April–September) and non-flood period (October–March) were completed using the discharge coefficient approach. The formula and data sources are listed in Table 1. Among these sources, most aquaculture waste water was discharged directly into surrounding rivers or aquaculture occurred directly in the rivers, thus the estimate of pollution discharge of aquaculture was calculated by discharge quantity uniformly, rather than distinguishing the two processes of pollution production and discharge.

**Table 1.** Source factors of nitrogen and phosphorus losses for agricultural non-point source pollution.

Formula	Parametric Description	Data Sources
<b>Agricultural Land</b>		
$Q_a = U_a \times A_a \times D \times C_a \times 10^{-3}$	$Q_a$ : The total load of N and P from agricultural land (kg)	Calculation result
	$U_a$ : Surface runoff amount per unit area of agricultural land, ( $\text{m}^3 \cdot \text{hm}^{-2} \cdot \text{d}^{-1}$ )	Calculated by precipitation [25]
	$A_a$ : The corresponding area size of agricultural land ( $\text{hm}^2$ )	Land use map by remote sensing analysis
	$D$ : Days in flood or non-flood period (d, day)	Local meteorological observatory data
	$C_a$ : The corresponding surface runoff concentration of N and P in agricultural land ( $\text{mg} \cdot \text{L}^{-1}$ )	Field data
<b>Domestic Discharge</b>		
$Q_r = \sum Q_{ri} = Q_{r1} + Q_{r2} + Q_{r3} = \sum N \times \frac{D \times P_{ri} \times V_{ri} \times C_{ri}}{10^{-3}}$	$Q_{r1}, Q_{r2}, Q_{r3}$ : N and P discharge load from rural domestic sewage, household rubbish, and human waste, respectively (kg)	Calculation result
	$N$ : The number of village resident population (p)	Local statistical yearbook
	$P_{ri}$ : Produce coefficient of N and P ( $\text{L} \cdot \text{p}^{-1} \cdot \text{d}^{-1}$ , $\text{kg} \cdot \text{p}^{-1} \cdot \text{d}^{-1}$ )	[13–15,24]
	$V_{ri}$ : Discharge coefficient (%)	
$C_{ri}$ : N and P content ( $\text{g} \cdot \text{L}^{-1}$ , $\text{g} \cdot \text{kg}^{-1}$ )		
<b>Livestock Breeding</b>		
$Q_l = \sum N_i \times D \times P_{li} \times V_{li} \times C_{li} \times 10^{-3}$	$Q_l$ : N and P discharge load from livestock breeding (kg)	Calculation result
	$N_i$ : The number of livestock breeding (p)	Local statistical yearbook
	$P_{li}$ : Produce coefficient of N and P ( $\text{kg} \cdot \text{p}^{-1} \cdot \text{d}^{-1}$ )	[17,18,24]
	$V_{li}$ : Discharge coefficient (%)	
$C_{li}$ : N and P content ( $\text{g} \cdot \text{L}^{-1}$ , $\text{g} \cdot \text{kg}^{-1}$ )		
<b>Aquaculture</b>		
$Q_a = \sum N_a \times D \times P_{ai}$	$Q_a$ : The total load of N and P from aquaculture (kg)	Calculation result
	$N_a$ : tons of various varieties of aquaculture production (t)	Local statistical yearbook
	$P_{ai}$ : Produce coefficient of N and P ( $\text{kg} \cdot \text{t}^{-1} \cdot \text{d}^{-1}$ )	[24]

### 2.2.2. Calculation of Migration Factors

Migration factor system is focused to evaluate the risk of nitrogen and phosphorus loss and the entrance into water by the effects of rainfall scouring in each pollution source [10]. The selection of

these factors, covering soil erosion, surface runoff, soil permeability, soil texture and distance from river, is based on impact factors of nitrogen and phosphorus loss from each agricultural non-point pollution source and the nitrogen and phosphorus loss evaluation index widely used worldwide.

Soil erosion is one of the most significant factors in agricultural nitrogen and phosphorus loss, and is calculated by soil erosion formula method (USLE) [26], the specific formula and calculation of which can be seen in an existing report [21]. Surface runoff is the primary hydrodynamic factor of soil nitrogen and phosphorus loss, and is calculated using the relationship formula of runoff and rainfall recorded by local hydrometric station during 30 years [25]. Soil permeability and soil texture play a vital role in both the output of nitrogen and phosphorus and the loss process of migration and transformation [10,11]. The size of soil particles can affect the soil permeability and retention capacity of surface runoff; besides, the stability of soil structure is the main basis of soil erosion resistance ability [22,27]. In particular, soil permeability factor is mainly applied for dissolved nitrogen and phosphorus. Nitrogen loss in Tiaoxi watershed is primarily dissolved status, where nitrate accounts for 59.3% of total nitrogen and is the main existing form of total nitrogen. The loss of phosphorus is mainly in particle status, accounting for 59.7% of total phosphorus, and is the primary composition of total phosphorus [20]. Therefore, the calculation of soil permeability factor usually refers to nitrogen loss. In this study, the classification of soil permeability factor and soil texture referred to corresponding reports with international classification of soil particle size [10,28]; relevant soil data were derived from Soil records of Zhejiang Province and Database of China Soil [29]. When the scale of pollution risk assessment of non-point source increased from field scale to watershed scale, the effect of distance between loss source and channel on the efficient input into water bodies was even more important, which is especially prominent for phosphorus loss in particle status, but less notable for nitrogen loss mainly in dissolved status [10,28]. The calculation of distance factor was to obtain the distribution value of channel distance in Tiaoxi watershed through the distance analysis function of ArcGIS, based on the distribution of water system generated by digital elevation model (DEM).

Migration factors were evaluated by qualitative assessment and divided into five types of risk level according to the actual value of each migration factor: very low, low, medium, high and very high, which were endowed as 0.2, 0.4, 0.6, 0.8 and 1, respectively. The weight assignment of migration factors was primarily operated according to the existing nitrogen and phosphorus loss assessment system [10,22,27], and modified according to local conditions of each source as well as expert opinions, which were finally normalized to make the sum of migration factor weight in the index system to be 1 (Table 2). The migration factor of aquaculture was defined as 1 by default due to the particularity, where the river, lake and pond were used as cultivation areas and the nitrogen and phosphorus load produced in waters directly.

**Table 2.** Migration factors of nitrogen and phosphorus losses for agricultural non-point source pollution.

Migration Factors	Weights		Rank Values				
	N	P	Very Low (0.2)	Low (0.4)	Medium (0.6)	High (0.8)	Very High (1)
<b>Agricultural Land</b>							
Soil erosion ( $t \cdot hm^{-2} \cdot a^{-1}$ )	0.2	0.3	<15	15–30	30–45	45–60	>60
Surface runoff depth (mm)	0.3	0.3	<500	500–900	900–1300	1300–1700	>1700
Soil permeation rate ( $mm \cdot h^{-1}$ )	0.3	-	<1.6	1.6–3.2	3.2–4.8	4.8–6.4	>6.4
Soil texture (Particle size, mm)	0.2	0.1	<0.04	0.04–0.07	0.07–0.10	0.10–0.13	>0.13
Contributing distance (m)	-	0.3	>8000	8000–6000	6000–4000	4000–2000	<2000
<b>Domestic Discharge and Livestock Breeding</b>							
Surface runoff depth (mm)	0.5	0.5	<500	500–900	900–1300	1300–1700	>1700
Contributing distance (m)	0.5	0.5	>8000	8000–6000	6000–4000	4000–2000	<2000

The migration factor of aquaculture = 1

Note: “-” indicates no such item factor.

### 2.2.3. Calculation of Nitrogen and Phosphorus Indices and Their Comprehensive Loss Risk Index

Nitrogen and phosphorus loss risk value for each pollution source is equal to the product of source and migration factors. Nitrogen loss comprehensive risk value and phosphorus loss comprehensive risk value are the sum of each risk value of pollution source, while nitrogen and phosphorus loss comprehensive risk value in watershed equals the mean value of normalized nitrogen risk and phosphorus risk.

#### (1) Nitrogen index calculation

The calculation formula of nitrogen loss risk value in each pollution source is:

$$N_{\text{index}} = \sum N_{si} \times N_{ti} = \sum N_{si} \times (\sum NW_{ij} \times NR_{ij}), \quad (1)$$

$N_{si}$  and  $N_{ti}$  are the source and migration factor index of nitrogen in agricultural non-point source of Case  $i$ , respectively (calculated by Table 1).  $NW_{ij}$  and  $NR_{ij}$  are the weight and risk level value of migration factor in Case  $j$  that correspond to the source in Case  $i$ , respectively [28].

#### (2) Phosphorus index calculation

The calculation formula of phosphorus loss risk value in each pollution source is:

$$P_{\text{index}} = \sum P_{si} \times P_{ti} = \sum P_{si} \times (\sum PW_{ij} \times PR_{ij}), \quad (2)$$

$P_{si}$  and  $P_{ti}$  are the source and migration factor index of phosphorus in agricultural non-point source of Case  $i$ , respectively (calculated by Table 1).  $PW_{ij}$  and  $PR_{ij}$  are the weight and risk level value of migration factor in Case  $j$  that correspond to the source in Case  $i$ , respectively [28].

#### (3) Calculation on nitrogen and phosphorus comprehensive index

The calculation formula of nitrogen and phosphorus comprehensive loss risk value in each pollution source is:

$$I_i = (P_{i1} + N_{i1})/2, \quad (3)$$

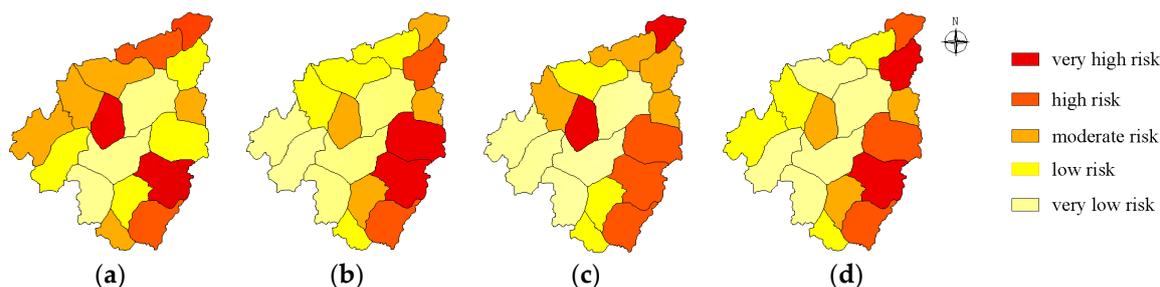
$N_{i1}$  and  $P_{i1}$  are the values of normalized nitrogen and phosphorus risk index, respectively [22].

## 3. Results and Discussion

### 3.1. Risk Assessment of Nitrogen, Phosphorus Loss and Their Comprehensive Loss in Flood Season

#### 3.1.1. Risk Assessment of Nitrogen Loss in Each Non-Point Source during Flood Season

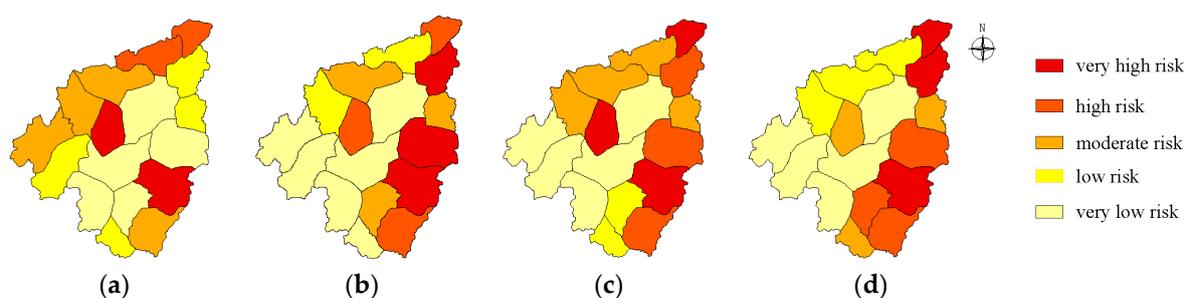
In Figure 2, during flood period, the nitrogen loss risk of agricultural non-point source in Tiaoxi watershed has a large difference in spatial distribution, and the distribution of nitrogen sources also varied. In particular, the sub-watersheds with high and relatively high risk of nitrogen loss from agricultural land were mainly distributed in the middle and lower reaches of West Tiaoxi and upper reaches of East Tiaoxi, where higher land reclamation level and more agricultural activities occur. Therefore, the distribution of intensive cultivated land and application of nitrogen fertilizer are the main reasons for the high nitrogen loss risk. Nitrogen loss risk of livestock breeding was mainly concentrated in the upper and middle reaches of East Tiaoxi. These areas are located in Deqing and Yuhang counties, where livestock breeding is comparatively developed. The dense distribution of river network also increased the risk of nitrogen loss from agricultural land and livestock breeding into the water. Nitrogen loss in domestic discharge was mainly distributed in the middle and lower reaches of watershed and the upstream of East Tiaoxi, where villages are densely distributed, and they are directly related to a lot of discharge of sewage and garbage. High and relatively high risk areas of nitrogen loss from aquaculture were concentrated in the lower reaches of West Tiaoxi around Taihu Lake and the middle reaches of East Tiaoxi.



**Figure 2.** N loss risk assessment of sub-watersheds for: agricultural land (a); livestock breeding (b); domestic discharge (c); and aquaculture (d) during flood period.

### 3.1.2. Risk Assessment of Phosphorus Loss in Each Non-Point Source during Flood Season

In Figure 3, during flood period, the phosphorus loss risk of agricultural non-point source in Tiaoxi watershed had a large difference in spatial distribution, and is different from the distribution of nitrogen loss risk. The high and relatively high risk sub-watersheds of phosphorus loss from agricultural land were mainly distributed in the upstream of Tiaoxi watershed, where the dense distribution of agricultural land and the application of phosphate fertilizer were the important reasons for the high phosphorus loss risk. The distribution of phosphorus loss risk was similar to that of nitrogen loss risk in livestock breeding, and the critical risk areas are mainly concentrated in the upper and middle reaches of East Tiaoxi, with an intensive distribution of livestock breeding in Deqing and Yuhang counties. The distribution of phosphorus loss for domestic discharge was similar to that of nitrogen loss as well, mainly present in the middle and lower reaches of West Tiaoxi and the upstream of East Tiaoxi. As a result, the density of population is the primary factor affecting the nitrogen and phosphorus loss risk for domestic discharge. Phosphorus loss risk in aquaculture was similar with nitrogen, in that the dense river network and ponds provided convenient conditions for aquaculture in high risk area. Meanwhile, the main reason for nitrogen and phosphorus input in these areas is attributed to the large scale of aquaculture, especially the soft-shelled turtle culture.

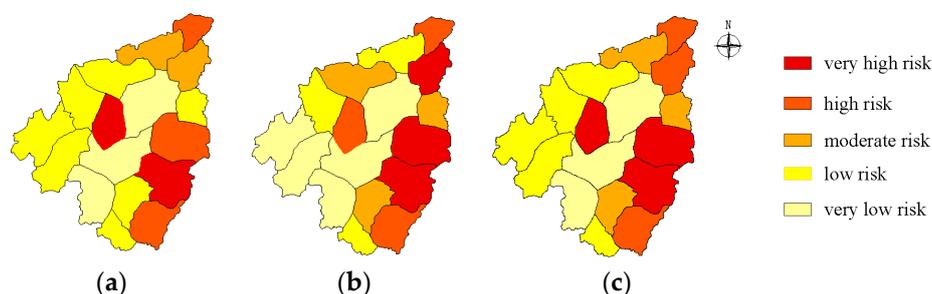


**Figure 3.** P loss risk assessment sub-watersheds for: agricultural land (a); livestock breeding (b); domestic discharge (c); and aquaculture (d) during flood period.

### 3.1.3. Risk Assessment of Nitrogen, Phosphorus Loss and Their Comprehensive Loss in Non-Point Source during Flood Season

Based on the data of distribution of nitrogen and phosphorus loss in agricultural land, livestock breeding, domestic discharge and aquaculture, this study described the distribution of nitrogen and phosphorus loss risk in the watershed, using the superposition of ArcGIS raster data, and also described the distribution of nitrogen and phosphorus comprehensive loss risk according to Formula (3). Basically, in Figure 4, for all pollution source of Tiaoxi watershed, the distribution of nitrogen and phosphorus comprehensive loss risk in major areas of watershed were low and relatively low risk region, which were widespread in West Tiaoxi catchment, while high and relatively high risk areas were mainly distributed in the part of East Tiaoxi catchment and the downstream of Tiaoxi

watershed. Thus, the spatial distribution of nitrogen and phosphorus loss risk of non-point source was discrepant.



**Figure 4.** Risk assessment of: N (a); and P (b) loss; and their comprehensive loss risk (c), during flood period.

### 3.1.4. Contribution Values of Each Source in Critical Risk Areas of Nitrogen and Phosphorus Pollution Risk during Flood Period

To further understand the reasons for high risk in critical risk areas, pollution source contributions of nitrogen and phosphorus loss in critical risk areas were analyzed (Table 3).

At critical risk areas of nitrogen loss, the nitrogen loss was mainly from agricultural land and livestock breeding, accounting for 30.85% and 36.18%, respectively. Among five sub-watersheds of nitrogen loss for critical risk areas, there were three sub-watersheds with agricultural land as the primary nitrogen loss source, and two sub-watersheds with livestock breeding. Domestic discharge and aquaculture occupied relatively low proportions of nitrogen loss risk within critical risk areas, accounting for only 17.67% and 15.29%, respectively.

At critical risk areas of phosphorus loss, phosphorus loss was mainly from livestock breeding (56.28%), and the primary phosphorus loss risk was as a result of livestock breeding in all six sub-watersheds of critical risk areas. Agricultural land, domestic discharge, and aquaculture occupied comparatively low proportions in phosphorus loss risk, accounting for only 14.38%, 15.92%, and 13.42%, respectively, of which the proportions were much lower than nitrogen loss risk of livestock breeding.

Overall, during flood season, the pollution risk source area of nitrogen and phosphorus were mainly from livestock breeding and agricultural land. Agricultural land and livestock breeding were the main nitrogen loss source, accounting for 30.85% and 36.18%, respectively. Primary phosphorus loss was mainly attributed to livestock breeding (56.28%).

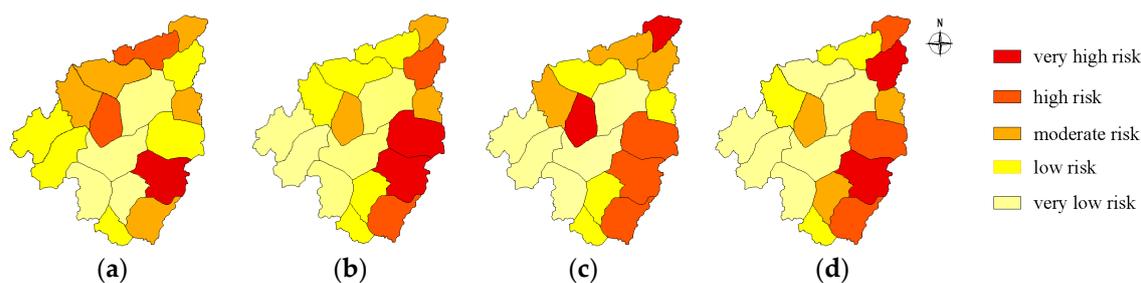
**Table 3.** Contribution values of each source in critical risk areas of N and P loss during flood period.

Sub-Watershed of Critical Risk Areas		Contribution Values of Different Pollution Source during Flood Period (%)			
(Risk from High to Low)		Agricultural Land	Livestock Breeding	Domestic Discharge	Aquaculture
N	14	21.35	53.56	8.8	16.29
	8	30.79	21.33	24.16	23.72
	17	34.66	31.89	19.81	13.64
	13	25.92	58.74	11.77	3.57
	1	41.54	15.39	23.82	19.25
Mean (5)		30.85	36.18	17.67	15.29
P	13	8.08	78	4.34	9.58
	14	8.6	76.25	8.68	6.47
	1	10.08	61.46	15.15	13.31
	8	25.31	27.22	28.76	18.71
	6	7.68	59.3	13.75	19.27
17	26.5	35.47	24.84	13.19	
Mean (6)		14.38	56.28	15.92	13.42

### 3.2. Risk Assessment of Nitrogen, Phosphorus Loss and Their Comprehensive Loss in Non-Flood Period

#### 3.2.1. Risk Assessment of Nitrogen Loss in Each Non-Point Source during Non-Flood Season

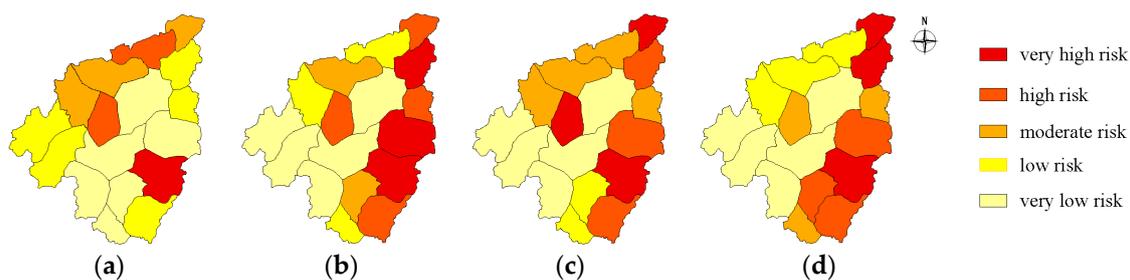
As shown in Figure 5, during the non-flood season, the nitrogen loss risk of agricultural non-point source in Tiaoxi watershed had a large difference in space and source distribution, but the spatial distribution of total nitrogen loss risk was similar to the pattern of flood season. The corresponding areas showed a certain amount of changes of risk level during non-flood period. In this distribution, the high and relatively high risk areas of agricultural land was lesser than that in flood period, but was still distributed mainly in the downstream of West Tiaoxi and the upstream of East Tiaoxi. It has been reported that the nitrogen and phosphorus pollution in agricultural land mainly stemmed from the application of fertilizer, and the amount of fertilizer used in non-flood period (autumn and winter) accounted for only 30.2% of that in the whole year [12], which led to the smaller value of source factor in agricultural land in non-flood period than that in flood period. In addition, during non-flood period, migration factors such as rainfall also had changed, and the migration of nitrogen and phosphorus would decrease. Thus, the total nutrient loss risk would decrease in agricultural land during non-flood period, while the high and relatively high risk areas of livestock breeding would increase. Previous research indicated that the production and discharge of nitrogen and phosphorus in excretion products such as feces and urine from hogs, sheep and rabbits in winter were much more than that in summer during the process of livestock breeding [16,17]. This should be the main reason for the increase of nitrogen pollution risk during non-flood season. High risk areas of nitrogen loss for domestic discharge showed larger areas in non-flood season than in flood season, which is relevant to nitrogen discharge coefficient (daily emission amount per person) of domestic sewage and refuse during different periods. It has been reported that the concentration and discharge coefficient of nitrogen and phosphorus for domestic sewage in flood season were smaller than those in non-flood season [13,14]. Besides, during the non-flood period, the influence of the major Chinese traditional festival—Spring Festival, whose activities lasts for half to almost one full month, gives rise to the remarkable increase of domestic sewage and garbage [15,30] and also the primary reason for the nitrogen loss risk during non-flood season. However, for other non-point source, aquaculture was less influenced by flood and non-flood period, with no significant change of nitrogen loss.



**Figure 5.** N loss risk assessment in: agricultural land (a); livestock breeding (b); domestic discharge (c); and aquaculture (d) during non-flood period.

#### 3.2.2. Risk Assessment on Phosphorus Loss of Non-Point Source during Non-Flood Season

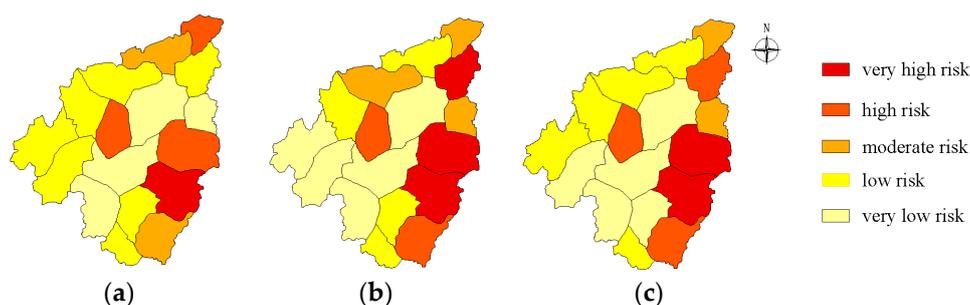
The distribution of phosphorus loss risk during non-flood period was akin to that during flood period in Tiaoxi watershed (Figure 6). Similar to nitrogen, the risk levels of corresponding areas were different in non-flood and flood period. In non-flood season, the phosphorus loss risk in agricultural land was reduced to a certain extent, but an opposite situation existed for livestock breeding and domestic discharge, while no significant variability was observed in aquaculture, which portended the temporal-spatial difference of nitrogen and phosphorus loss risk for agricultural non-point source.



**Figure 6.** P loss risk assessment for: agricultural land (a); livestock breeding (b); domestic discharge (c); and aquaculture (d) during non-flood period.

### 3.2.3. Risk Assessment of Nitrogen and Phosphorus Loss and Comprehensive Lpss Risk during Non-Flood Season

In Figure 7, the distribution of nitrogen, phosphorus and their integrated loss risk during non-flood period was similar to the pattern of flood period. The relatively high and high risk areas were still scattered mainly in parts of East Tiaoxi catchment and the downstream of this watershed, however, the whole regional risk was low. Therefore, the nutrition loss of non-point source has the characteristic of spatial-temporal differentiation in watershed.



**Figure 7.** Risk assessment of: N (a); and P (b) loss; and their comprehensive loss risk (c), during non-flood period.

### 3.2.4. Contribution Values of Each Source in Critical Risk Areas for Nitrogen and Phosphorus Loss during Non-Flood Season

In Table 4, the contribution sources of critical risk areas of nitrogen loss risk were mainly livestock breeding and domestic discharge, taking up 43.37% and 22.18%, respectively, during non-flood period. Among the four sub-watersheds of critical risk area of nitrogen loss, there were two sub-watersheds where the primary nitrogen loss sources were the livestock breeding and domestic discharge. Compared with flood season, the situation of nitrogen loss from livestock breeding and domestic discharge was prominent in non-flood period.

Among critical risk areas of phosphorus loss, most of phosphorus loss was from livestock breeding, representative of the primary pollution source in each sub-watershed of critical risk areas, accounting for 58.31% of the average source contribution. This was followed by the domestic discharge (22.06%), while aquaculture and agricultural land occupied the lowest proportions for phosphorus loss risk, only 14.53% and 6.87%, respectively.

Overall, during non-flood period, much attention must be paid to the integrated management of livestock breeding and domestic discharge in order to control the nitrogen loss of critical risk area. Moreover, the management of livestock breeding should also be combined with domestic discharge pollution when controlling the phosphorus loss in critical risk area. However, specific comprehensive management of nitrogen and phosphorus loss control in sub-watershed is supposed

to be implemented in the primary areas of different sub-watershed in order to establish the pivotal measures of management and control for each pollution source.

**Table 4.** Contribution values of each component in critical risk areas of N and P pollution during non-flood period.

Sub-Watershed of Critical Risk Areas		Contribution Value of Different Pollution Source during Non-Flood Period (%)			
(Risk from High to Low)		Agricultural Land	Livestock Breeding	Domestic Discharge	Aquaculture
N	14	10.59	59.32	11.83	18.26
	8	20.32	26.59	28.31	24.78
	1	23.34	24.85	30.58	21.23
	13	13.57	62.70	17.99	5.74
Mean (4)		16.96	43.37	22.18	17.50
P	6	5.27	59.95	15.10	19.68
	13	4.08	79.08	6.34	10.50
	14	6.40	75.65	11.28	6.67
	8	9.76	31.72	38.21	20.31
	17	8.86	45.14	39.37	15.49
Mean (5)		6.87	58.31	22.06	14.53

#### 4. Summary and Conclusions

Due to the changes of natural climate, hydrology and anthropogenic activities, the soil nitrogen and phosphorus have different source and migration factors during flood and non-flood seasons. This can be figured out using index system method to assess the spatial-temporal distribution characteristics of nitrogen, phosphorus loss and their comprehensive loss risk in Tiaoxi watershed with primary agricultural non-point source. Besides, the critical risk areas of nitrogen and phosphorus loss and their source contributions in Tiaoxi watershed can be identified. Accordingly, it is of great practical significance to propose spatial-temporal targeted measurements to control nitrogen and phosphorus pollution for the hilly-plain watershed in China.

According to the analyzed results in this context, during flood season, the critical risk sources of nitrogen and phosphorus loss in Tiaoxi watershed were dominated by agricultural land and livestock breeding. In addition, the nitrogen loss sources were mainly accounted for by agricultural land and livestock breeding (30.85% and 36.18%, respectively), while the phosphorus loss mainly came from livestock breeding (56.28%).

In the non-flood period, the high and relatively high risk areas of nitrogen and phosphorus loss for agricultural land was less compared to the flood period, but were still concentrated in the downstream of West Tiaoxi and the upstream of East Tiaoxi. For critical risk areas, livestock breeding and domestic discharge remained the major source of nitrogen loss, accounting for 43.37% and 22.18%, respectively, while the nitrogen loss from livestock breeding was more prominent in non-flood season. Meanwhile, the proportion of phosphorus loss from livestock breeding was remarkable, accounting for 58.31% of average source contribution, and represented the primary source for each sub-watershed of critical risk areas. Therefore, the loss of nitrogen and phosphorus from livestock breeding should be given attention in the non-flood season.

Based on the spatial distribution characteristics of nitrogen and phosphorus loss risk, we conclude that nitrogen and phosphorus loss risk was weaker in West Tiaoxi catchment than in East Tiaoxi catchment. N and P pollution in West Tiaoxi catchment was mainly concentrated at the middle and lower reaches and originated from agricultural land. In the upstream of East Tiaoxi, N and P pollution was mainly attributed to agricultural land, livestock breeding and domestic discharge, whereas for the middle reaches, these nutrients mainly emerged from livestock breeding and aquaculture. Based on this, we recommend that further studies should try to establish effective relationships between the loss sources and water quality whiles taking targeted measures to control N and P pollution according to their changes of loss risk in watershed.

**Acknowledgments:** This research was supported by National Natural Science Foundation of China (41372354), the National Key R&D Program of China (2017YFD0800302) and the Priority Academic Program Development of Jiangsu Higher Education Institutions (PPZY2015A051). The authors would like to thank Haiyan Xu, Zhengyang Li and Jing Jin for their fieldwork support. We are grateful to Rui Zhou for laboratory work.

**Author Contributions:** Xuyin Yuan and Hongmeng Ye proposed the research framework and draft the paper. Lei Han, Ja Bawk Marip, and Jing Qin worked on the analysis, interpretation of results and discussion. The further revision work was carried out by Hongmeng Ye, Xuyin Yuan, and Ja Bawk Marip. All the authors have read and approved the final manuscript.

**Conflicts of Interest:** The authors declare no conflicts of interest.

## References

1. Corwin, D.L.; Vaughan, P.J.; Loague, K. Modeling nonpoint source pollutants in the vadose zone with GIS. *Environ. Sci. Technol.* **1997**, *31*, 2157–2175. [[CrossRef](#)]
2. Fraga, I.; Charters, F.J.; O’Sullivan, A.D.; Cochrane, T.A. A novel modelling framework to prioritize estimation of non-point source pollution parameters for quantifying pollutant origin and discharge in urban catchments. *J. Environ. Manag.* **2016**, *167*, 75–84. [[CrossRef](#)] [[PubMed](#)]
3. Ding, X.; Shen, Z.; Hong, Q.; Yang, Z.; Wu, X.; Liu, R. Development and test of the export coefficient model in the upper reach of the Yangtze River. *J. Hydrol.* **2010**, *383*, 233–244. [[CrossRef](#)]
4. Liu, Z.; Chao, J.Y.; Zhang, L.; Jie, Y.F.; Zhang, W.; He, W. Current status and problems of non-point source pollution load calculation in China. *Adv. Water Sci.* **2015**, *26*, 432–442. (In Chinese)
5. Ongley, E.D.; Xiao, L.Z.; Tao, Y. Current status of agricultural and rural non-point source pollution assessment in China. *Environ. Pollut.* **2010**, *158*, 1159–1168. [[CrossRef](#)] [[PubMed](#)]
6. Ministry of Environmental Protection of China. Bulletin of the first national census of pollution sources. *The People’s Daily*, 10 February 2010; 16. (In Chinese)
7. Ulén, B.; Stenberg, M.; Wesström, I. Use of a flashiness index to predict phosphorus losses from subsurface drains on a Swedish farm with clay soils. *J. Hydrol.* **2016**, *533*, 581–590. [[CrossRef](#)]
8. Bolster, C.; Vadas, P.; Boykin, D. Parameter uncertainty analysis for the annual phosphorus loss estimator (APLE) model. *J. Hydrol.* **2016**, *539*, 27–37. [[CrossRef](#)]
9. Cherry, K.A.; Shepherd, M.; Withers, P.J.A.; Mooney, S.J. Assessing the effectiveness of actions to mitigate nutrient loss from agriculture: A review of methods. *Sci. Total Environ.* **2008**, *406*, 1–23. [[CrossRef](#)] [[PubMed](#)]
10. Drewry, J.J.; Newham, L.T.H.; Greene, R.S.B. Index models to evaluate the risk of phosphorus and nitrogen loss at watershed scales. *J. Environ. Manag.* **2011**, *92*, 639–649. [[CrossRef](#)] [[PubMed](#)]
11. Heckrath, G.; Bechmann, M.; Ekholm, P.; Ulén, B.; Djodjic, F.; Andersen, H.E. Review of indexing tools for identifying high risk areas of phosphorus loss in Nordic watersheds. *J. Hydrol.* **2008**, *349*, 68–87. [[CrossRef](#)]
12. Yang, F.; Meng, Y.D.; Yang, Y.; Cui, Y.; Li, R.; Dong, Y.; Sun, Z. Chemical fertilizer application and supply in crop farming in China in 2013. *J. Plant Nutr. Fertil.* **2015**, *21*, 217–225. (In Chinese)
13. Zhu, H.; Li, H.Z.; Ye, J.F.; Fu, W. Coefficients of major pollutants in domestic sewage in Shanghai. *China Environ. Sci.* **2010**, *30*, 37–41. (In Chinese)
14. Chen, J.C.; Liu, S.Y.; Peng, X.Y. Countermeasures and suggestions about rural sewage pollution in Changshou Lake watershed in Chongqing Province. *Modem Agric. Sci.* **2008**, *25*, 94–98. (In Chinese)
15. Yuan, X.Y.; Yu, Z.M.; Shi, W.M. Domestic sewage emission dynamics and pollutant loading capacity of the Daqing River valley: A case study on the village scale. *J. Agro-Environ. Sci.* **2010**, *29*, 1547–1557. (In Chinese)
16. Guo, D.J.; Wu, H.S.; Ma, Y.; Chan, Z.Z. Study on the amount of manure and urine excreted by sheep and rabbits in intensive pasture. *J. Ecol. Rural Environ.* **2011**, *27*, 44–48. (In Chinese)
17. Guo, D.J.; Wu, H.S.; Ma, Y.; Chan, Z.Z.; Xu, Y.D.; Zhang, J.Y. Monitoring of the amount of pig manure and urine in different swineries. *Jiangsu J. Agric. Sci.* **2011**, *27*, 516–522. (In Chinese)
18. Sharpley, A.; Tunney, H. Phosphorus research strategies to meet agricultural and environmental challenges of the 21st century. *J. Environ. Qual.* **2000**, *29*, 176–181. [[CrossRef](#)]
19. Jin, J.L.; Wang, F.E.; Dai, L.Y.; Yu, J.; Tian, P.; Zhang, Z.J. Characteristics of non-point source pollution in Tiaoxi watershed and related affecting factors. *Chin. J. Appl. Ecol.* **2011**, *22*, 2119–2125. (In Chinese)
20. Nie, Z.Y.; Liang, X.Q.; Xing, B.; Ye, Y.S.; Qian, Y.C.; Yu, Y.W.; Bian, J.Y.; Gu, J.T.; Liu, J.; Chen, Y.X. The current water trophic status in Tiaoxi River of Taihu Lake watershed and corresponding coping strategy based on N/P ratio analysis. *Acta Ecol. Sin.* **2012**, *32*, 48–55. (In Chinese)

21. Dai, L.Y.; Wang, F.E.; Yu, J. Assessing soil erosion potential using GIS for a typical watershed in East-Tiaoxi Basin, China. *J. Agro-Environ. Sci.* **2012**, *31*, 1777–1784. (In Chinese)
22. Bechmann, M.; Stålnacke, P.; Kværnø, S.; Eggestad, H.O.; Øygarden, L. Integrated tool for risk assessment in agricultural management of soil erosion and losses of phosphorus and nitrogen. *Sci. Total Environ.* **2009**, *407*, 749–759. [[CrossRef](#)] [[PubMed](#)]
23. Ekholm, P.; Turtola, E.; Grönroos, J.; Seuri, P.; Ylivainio, K. Phosphorus loss from different farming systems estimated from soil surface phosphorus balance. *Agric. Ecosyst. Environ.* **2005**, *110*, 266–278. [[CrossRef](#)]
24. Hu, C.X.; Zhou, L.J.; Huang, Z.Q.; Zhang, Z.M. Comprehensive evaluation of water pollution caused by agricultural non-point source in Tiaoxi River. *Acta Agric. Zhejiangensis* **2011**, *23*, 1199–1202. (In Chinese)
25. Wischmei, W.H.; Johnson, C.B.; Cross, B.V. Soil erodibility nomograph for farmland and construction sites. *J. Soil Water Conserv.* **1971**, *26*, 189–193.
26. Li, Z.F.; Yang, G.S.; Li, H.P. Influence of land use on nitrogen exports in Xitiaoxi typical sub-watersheds. *China Environ. Sci.* **2005**, *25*, 678–681. (In Chinese)
27. Lemunyon, J.; Gilbert, R.G. The concept and need for a phosphorus assessment tool. *J. Prod. Agric.* **1993**, *6*, 483–486. [[CrossRef](#)]
28. McDowell, R.W.; Sharpley, A.N.; Kleinman, P.J. Integrating phosphorus and nitrogen decision management at watershed scales. *JAWRA J. Am. Water Resour. Assoc.* **2002**, *38*, 479–491. [[CrossRef](#)]
29. Wu, J.P.; Hu, Y.L.; Zhi, J.J.; Jing, C.W.; Chen, H.J.; Xu, J.; Lin, S.P.; Li, D.; Zhang, C.; Xiao, R.; et al. A 1:50,000 scale soil database of Zhejiang Province, China. *Acta Pedol. Sin.* **2013**, *50*, 30–40. (In Chinese)
30. Butler, D.; Friedler, E.; Gatt, K. Characterising the quantity and quality of domestic wastewater inflows. *Water Sci. Technol.* **1995**, *31*, 13–24.



© 2017 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).