sustainability

MDPI

Article

Application of Export Coefficient Model and QUAL2K for Water Environmental Management in a Rural Watershed

Zhuohang Xin, Lei Ye * and Chi Zhang

School of Hydraulic Engineering, Dalian University of Technology, Dalian 116024, China; xinzh@dlut.edu.cn (Z.X.); zhangxiaojing@mail.dlut.edu.cn (C.Z.)
* Correspondence: yelei@dlut.edu.cn

Received: 16 October 2019; Accepted: 28 October 2019; Published: 30 October 2019

check for updates

Abstract: Water quality deterioration caused by excessive nutrient discharge from various point and non-point sources are a global challenge. Understanding the pollution sources and their respective contribution is the prerequisite for environmental planning, management and restoration. In this study, the influence of complex pollution sources on the water quality of the Dengsha River watershed in Dalian, China, was investigated. The export coefficient method was coupled with the QUAL2K water quality model to estimate the loads of ammonia nitrogen (NH_4-N) and total phosphorus (TP) from different sources, and to explore their respective contributions. Results indicated that animal feedlot and crop production were major sources for NH_4-N load, and crop production, soil erosion and animal feedlot are the largest three sources of TP load with an annual total contribution of 98.4%. The pollutant load exhibited an intra-annual variation mainly due to the seasonality of rainfall and anthropogenic agricultural activities. The overall waste assimilation capacity (WAC) is overloaded and suggestions for water pollution control and treatment regarding each pollution source were proposed. This study addressed a new application of QUAL2K model coupled with the export coefficient model for watershed managers towards a sustainable water environmental management, and can therefore be a reference example for other small and medium-sized rural watersheds.

Keywords: water quality deterioration; export coefficient model; QUAL2K; water environment governance; China

1. Introduction

Water environment issues associated with rapid economic development have become one of the most critical concerns facing both the national and local governments in many regions of the world [1,2]. Anthropogenic activities (e.g., urbanization, industry, agriculture and dam construction) accompanied by natural processes (e.g., precipitation, runoff and erosion) have caused problems such as low water quality, serious water ecological damage and varied environmental risks, threatening people's health and sustainable economic and social development [3,4].

Particularly in China, a country with nearly half of its population living in rural areas, the domestic sewage from rural households, and from animal feedlots are hardly treated before being drained into the water body. In addition, the rapid economic development and expectant population increase have anticipated an ever-growing demand for industrial products, agriculture yield and pollutant emission. Under the requirement of rapid economic development, as well as the rising public desire for a better ecosystem, the Chinese government has implemented a series of comprehensive policies to safeguard the nation's waters, such as the Action Plan for Water Pollution Prevention and the River Chief System issued by the State Council in 2015 and 2016, respectively [5]. These are not independent plans but amalgamations of other plans and policies with wide-ranging impact across sectors. However, implementation of these policies and effective water quality improvement measures need a sound understanding of the pollution sources and their respective contribution to the water quality deterioration [6,7]. For this, the water quality model can be an effective tool for simulating the pollutant migration and transportation processes from various point and non-point sources [8–10].

A variety of models with various complexities have been developed and used, from the empirical to conceptual and finally physically based models [11,12]. Empirical models such as export coefficients model, artificial neural network and fuzzy regression model, are data-driven models that involve mathematical equations between inputs and outputs and do not consider the features and processes of the hydrological system [13–15]. This type of model is relatively simple and has minimal data requirements. Conceptual models like GREEN [16] and MONERIS [17] use semi empirical equations and require several hydrological, meteorological and water quality data. The process-based models, however, can explicitly represent the mechanisms and physical processes in the real system such as the soil and water assessment tool (SWAT) [10,18], agricultural non-point source pollution model (AGNPS) [19], MIKE-11 [13] and QUAL2K [20]. Among these, the QUAL2K model has been applied worldwide in evaluating river water quality and estimating the impacts of pollutant on water quality indicators [21–26]. Due to its popularity and ease of application, the QUAL2K model is chosen for in-stream water quality simulation in this study, and the export coefficients model is coupled for estimating the pollutant load drained into the water body.

The aim of this study was to achieve a deeper understanding of the pollutant loads from various terrestrial sources and their contributions to the water quality variations. The case study of the Dengsha River watershed in Dalian, China, was analyzed. The specific objectives were: (1) to estimate the pollutant loads (i.e., NH_4-N and TP) yielded by various terrestrial sources using the export coefficient model, including industries, animal feedlots, crop production, rural household and natural soil erosion; (2) to quantify the relative contribution of each pollution source to the river water quality variation in both temporal and spatial scales, using the QUAL2K model and (3) to propose suggestions for the local water pollution control and governance. This study not only contributes to improving the water quality in the study region, but also offers an example of applying the simple water quality models for informed decision-making to ensure sustainable water environment planning and management.

2. Materials and Methods

2.1. Study Area

This study is focused on the Dengsha River watershed (Figure 1), which falls within the administrative boundary of the Jinzhou New District of Dalian City, Liaoning Province, China, with a drainage area of approximately 229 km^2. The Dengsha River has a total length of 25.7 km that originates from the upstream mountainous region, passing through three sub-districts of Jinzhou New District, and eventually empties into the Yellow Sea. The region has a warm temperate zone continental monsoon climate with annual mean air temperature of 11 °C and annual mean precipitation of 510 mm. Precipitation is unevenly distributed throughout the year with more than 70% of precipitation occurring during flood season from July to September. The Dengsha River is an ephemeral river that may cease to flow during the dry season of the dry year; the average annual runoff and flow rate are about 0.51×10^9 m^3 and 0.95 m^3/s, respectively.

The study region was predominantly agricultural land covering nearly 70% of the total area, most of which is used for corn and wheat. Rural residence and forest cover 19% and 6% of the total area, respectively; while other lands occupy the remaining less than 5%. The region has traditionally played an important role in the economic growth of Dalian City. The socioeconomic structure gives priority to crop production and animal breeding in the upper and middle areas, while industrial factories are scattered in the downstream area (Figure 1). Similar to many other rural areas in China, the water treatment facilities such as sewage pipe networks and wastewater treatment plants are not well equipped in the study region, thus the domestic sewage, agricultural surface runoff, animal wastewater and industrial effluent are directly discharged into the environment and water body, which are primary pollution sources of the river and have resulted in severe water quality deterioration. During the study period from 2014 to 2015, there was one wastewater treatment plant being constructed that has not been put into operation, thus it was not considered in the model simulation.

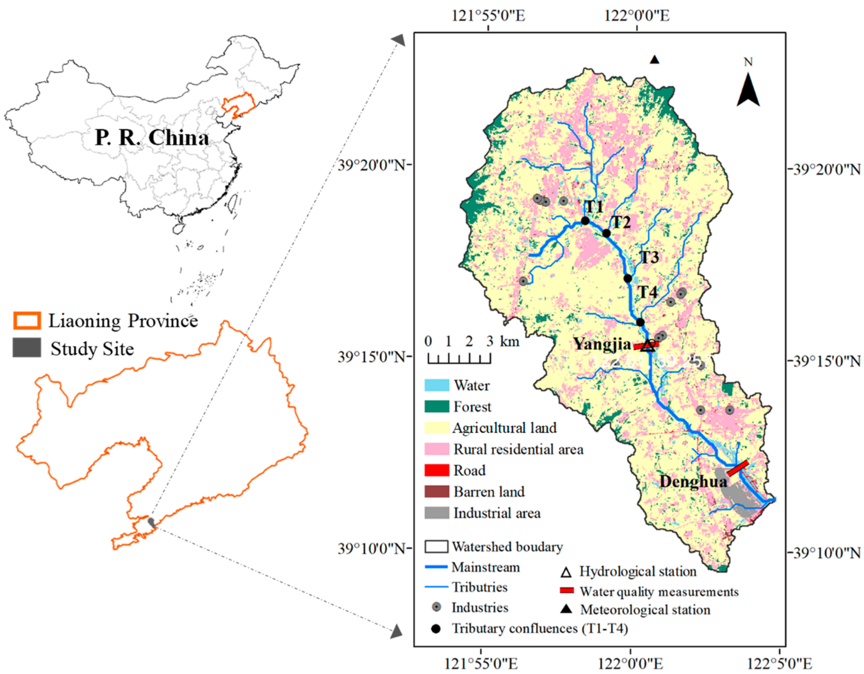


Figure 1. Map of the Dengsha River watershed showing the river system, and locations of industries, hydrological station, meteorological station and water quality measurements.

According to the published water quality data from Dalian Environment Quality Bulletin and Environmental Protection Bureau of Liaoning Province, the water quality at the middle-stream section of Yangjia and downstream section of Denghua (Figure 1) are most of the time below the prescribed Categories III and IV, respectively, of the Chinese Surface Water Quality Standard (GB 3838-2002) [27]. The standard specifies of a total of five categories (I to V) of water bodies, among which, Category III can be used for fisheries and swimming, while Category IV can be only used for industrial production and human amusement without direct body contact. Considering the specific utilizable functions of the water body, different categories are applied to the middle and downstream sections of the Dengsha River. NH_4-N and TP are of the major excessive factors in the river and are therefore selected as target pollutants in this study. Understanding how the various sources contribute to the excessive concentrations of pollutants is the prerequisite to implementing effective water quality improvement countermeasures in such a small basin with complex pollution sources.

2.2. Data Source

The river geometry, such as width, elevation and bottom slope were acquired primarily from the Hydrological Bureau of Liaoning Province. Additionally, an oblique aerial survey was conducted at a 10-cm pixel resolution during November 1–3, 2018, by the research team; the river had a low flow condition during the survey dates with several river segments ceasing to flow, thus the surface elevation information at these cross sections were used as ancillary data for mapping the river geometry. Daily streamflow at the hydrological station of Yangjia was obtained from the Hydrological Bureau of Liaoning Province. Headwater flows and tributary inflows were generated by a SWAT model developed in the same region (unpublished data). Daily records of rainfall, air temperature, relative humidity and wind speed at the Jinzhou meteorological station from 2014 to 2015 were acquired from the China Meteorological Administration. Monthly measurements of NH_4-N and TP concentrations at the Yangjia and Denghua sections from 2014 to 2015 were obtained from the Bureau of Environmental Protection of Dalian City. Monthly loads of NH_4-N and TP were then estimated by multiplying the measured concentration with monthly streamflow.

The crop production, animal feedlot, rural household, industrial activity and natural erosion are primary sources responsible for the deterioration of water quality in the study region. As the sewage and wastewater have not been collected for central treatment, those from household use and animal feedlots are treated as non-point source pollution in this study; while the effluent from industries is treated as point source pollution.

Data were collected for the estimation of pollutant loads that drained into the river. Annual emissions of wastewater amount and NH_4-N load from 16 industrial factories were obtained from the Bureau of Environmental Protection of the Dalian City. The rural population of three sub-districts was obtained from the Statistical Yearbook of the Jinzhou New District. The average household sewage discharge was set to 50 L/d per capita, and the NH_4-N and TP loads were set to 4.0 g/d and 0.2 g/d per capita, respectively, according to the Technical Guidelines of National Water Environmental Capacity [28]. There were nearly one hundred animal feedlots in the study area; the population of breeding animals, including pig, chicken, duck and cow, for each feedlot was available from the Statistical Report of Bureau of Environmental Protection of the Jinzhou New District. The pollutant load emissions from all categories of animals were converted to the equivalent amount of pig (e.g., 30 chickens is equivalent to one pig), and the NH4-N and TP loads from one pig was set to 10 g/d and 2 g/d, respectively [28]. The area of the cropland was recorded by the Statistical Yearbook of the Jinzhou New District. Face-to-face interviews with six farmers from the upstream to downstream farmlands were conducted to collect information on crop management practices, e.g., the timing and amount of fertilizer application. The farming normally starts in early May, and the average fertilizer application rate over the cropland of the study region was about 450 kg/ha per year, which comprised of 195 kg/ha of nitrogen fertilizer, 215 kg/ha of phosphorus fertilizer, and 40 kg/ha of others. The loss rates of NH_4-N to the nitrogen fertilizer, and TP to the phosphorus fertilizer that entered the surface water were acquired for the study region from the First National Survey of Pollution Sources Bulletin of China [29], as 0.21% and 0.27%, respectively.

The 90 m digital elevation model (DEM) data provided by the NASA's Shuttle Radar Topography Mission (SRTM) was used to derive the slope over the study region. The soil types and properties were obtained from the soil databases of Institute of Soil Science, Chinese Academy of Sciences. The land use condition (in 2015) was obtained through digitalizing and interpreting the Landsat Thematic Mapper (TM) image, which can be obtained from the US Geological Survey Earth Resources Observation and Science (EROS) Center. These data were used as reference information for correcting the parameters when calculating the pollutant load from various sources (Section 2.3).

2.3. Pollutant Load Estimation

NH_4-N and TP loads from all known sources including industry, crop production, rural household, animal feedlots and natural soil erosion were considered in this study. The non-point source pollutants can be classified into the dissolved and adsorbed categories, depending on whether they are generated and transported by runoff or soil erosion [30,31].

For the dissolved pollutants, a unit-based model, which is adapted from the improved export coefficient method [15,31,32], is applied for estimating the NH_4-N and TP loads. The model calculates the total nutrient loads as the sum of the losses from individual sources and builds direct links between pollution sources and nutrient release through empirical data and coefficients [33], which is expressed as:

$$L_d = \sum_{i=1}^{n} \alpha_i E_i[A_i(I_i)], \quad (1)$$

where L_d is dissolved pollutant load (kg), i is the type of pollution sources, i.e., rural household, animal feedlot and crop production. E_i is the export coefficient for nutrient source i (kg/ca or kg/km^2), A_i is the population, or number of animals or area of cropland (km^2), I_i is the input of nutrients to source i (kg) and α_i is the loss rate of pollutants from source i into the river. Since precipitation and topography are the primary factors that affect the non-point source pollution [32], the values of α_i were corrected mainly with two considerations: (1) the spatial heterogeneity of slope and soil type and (2) the temporal variation of intra-annual streamflow, according to Chinese Academy for Environmental Planning (CAEP) [28] and Ding et al. [32]. Therefore, values of α_i varied in both temporal and spatial scales, which were determined as 0.05%–0.14% for rural household, 0.02%–0.11% for animal feedlot and 0.21%–0.27% for crop production, respectively, during the two-year study period throughout the whole watershed. All values lay within the reasonable range compared with previous studies [30–32].

Adsorbed pollutants are attached to, and transported by soil particles during soil erosion processes, which is estimated by the following formula [30,31]:

$$L_a = A \times C_s \times D_r \times \eta \times U, \tag{2}$$

where L_a is the adsorbed load from natural soil erosion (kg), C_s is the background content of adsorbed pollutants in soil (g/kg), which is determined from the soil testing results at ten sampling points over the study region, D_r is the sediment delivery ratio representing the ratio of measured sediment transport to total soil erosion, η is the enrichment ratio of the pollutants in soil, U is the area (ha) and A is the soil loss per unit area (t/ha), which can be calculated on the basis of Revised Universal Soil Loss Equation (RUSLE) [34,35]:

$$A = R \times K \times LS \times C \times P, \tag{3}$$

where R is the rainfall erosivity factor (MJ·mm·ha^{-1}·h^{-1}), K is the soil erodibility factor (t·ha·h·ha^{-1}·MJ^{-1}·mm^{-1}), LS is the slope length and slope steepness factor, C is the cover management factor and P is the conservation support practices factor. The values of parameters in Equations (2) and (3) were determined from previous studies and soil testing, as listed in Table 1. Note that the range of each parameter indicated a temporal–spatial variation due to the heterogeneity of slope and soil type, as well as the variation of intra-annual precipitation.

Table 1. Methods for estimating the parameters in Equations (2) and (3), and their values in the Dengsha River watershed.

Parameter	Unit	Method	Value
C_s	g/kg	China Soil Database; Soil testing	NH_4-N: (2.24–2.82) × 10^{-3} TP: 0.02–0.4
D_r	—	Didoné et al. [36]; Gao et al. [37]	0.04–0.18
η	—	Guo et al. [38]	1.01–1.20
R	MJ·mm·ha^{-1}·h^{-1}	Wischmeier and Smith [39]	0–1640.70
K	t·ha·h·ha^{-1}·MJ^{-1}·mm^{-1}	Wischmeier [40]	0.01–0.02
LS	—	Liu et al. [41]; Wischmeier and Smith [39]	0–64.00
C	—	Cai et al. [42]	0–0.31
P	—	Chen et al. [43]	0–0.25

2.4. QUAL2K Model

As the pollutant loads estimated from the export coefficient method cannot directly address the in-stream pollutant transport and retention [44,45], the QUAL2K model was further coupled to simulate these processes and their impacts on water quality in the main river.

QUAL2K is a one-dimensional river and stream water quality model, which was developed by the US Environmental Protection Agency [20]. The model allows users to segment the river into several reaches and further divide each reach into a series of equally spaced elements, which are fundamental computational units of the model. The flow is considered steady, which is non-uniform, and the lateral inflows and withdrawals, as well as multiple pollutant loadings from both the point source and non-point source can be added into any element. The model is applicable to the streams that are laterally and vertically well-mixed, thus advection and dispersion are assumed only to occur along the main flow direction (longitudinal direction).

A steady-state flow balance is implemented for each model element. Once the flow of an element has been solved, the velocity and depth are calculated using the empirically derived rating curves as proposed by Leopold and Maddock [46]:

$$U = aQ^b,\ H = \alpha Q^\beta, \tag{4}$$

where U is flow velocity (m/s), Q is flow rate (m^3/s), H is water depth (m) and a, b, α and β are empirical coefficients that can be determined from the hydraulic measurements and river geometry.

The model can simulate the migration and transformation processes of a wide variety of constituents including inorganic suspended solids, dissolved oxygen, ammonia nitrogen, nitrate nitrogen, total nitrogen, organic phosphorus, inorganic phosphorus, phytoplankton and algae. A general mass balance is applied for all water quality constituents but the bottom algae variables within the reach, considering the dispersion, advection, chemical reaction, external load import, sinks and sources. Details on interactions of various state variables and model equations can be found in the literature [20–22].

2.5. Model Application

In the application of the QUAL2K model in the Dengsha River, the entire length of the river was divided into six reaches considering the water quality and hydraulic characteristics. Each reach was further divided into a series of 0.5 km-length elements, resulting in 39 computational units in the model. Point source emissions from 16 factories were added to the corresponding elements according to their locations, and non-point source was input as line source, which was demarcated by the starting and ending points. Figure 2 showed the schematic of the reaches, elements and additions of pollution sources. River geometries and measurements of flow velocity, flow rate and water depths at several sections were used to estimate the coefficients of a, b, α and β in Equation (4), which were determined as 0.52, 0.43, 0.12 and 0.45, respectively. Headwater flows and tributary inflows were given as boundary conditions, and meteorological data were used to drive the model.

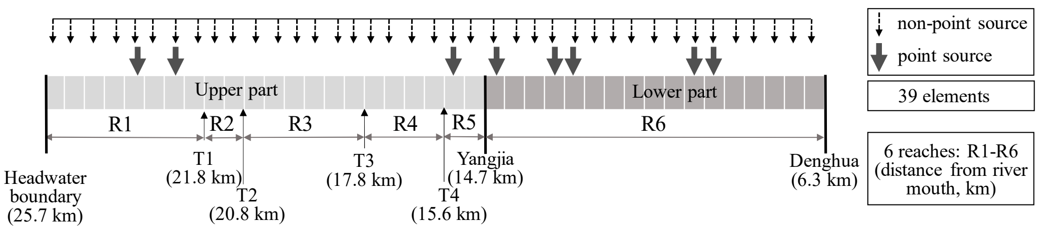


Figure 2. Schematic representation of the reaches, elements and pollution sources of the Dengsha River (see Figure 1 for notations of T1–T4).

With the above settings and inputs, the water quality parameters were calibrated to the observed NH_4-N and TP loads at Yangjia and Denghua sections from 2014 to 2015, based on the trial and error method. The coefficient of determination (R^2) [47] was used as the objective function to evaluate the model performance.

The QUAL2K model was then applied to identify the NH_4-N and TP load contribution from each pollution source. The watershed was divided into two parts considering the distribution of terrestrial pollution sources and location of river water quality measurements: the upper part from the head source to Yangjia section, and the lower part from Yangjia to Denghua section. As a baseline scenario, the model was firstly run with only the crop production source as input, yielding NH_4-N and TP loads from this sole source. Then the model was run under the combined effects of crop production and other individual pollutant source by adding each source once a time, the difference between which and the baseline scenario was calculated as the load from the added individual pollutant source, and so forth, the NH_4-N and TP loads contributed by cropland surface runoff, industrial wastewater, rural household sewage, animal feedlot and soil erosion were obtained.

3. Results

3.1. Estimation of Pollutant Loads from Various Sources

The NH_4-N and TP loads generated by different pollution sources were estimated using the export coefficient model, as shown in Table 2. According to the results, the annual NH_4-N load from the study region was 32.9 t, of which 71.7% was from the upper part, and 28.3% was from the lower part. The total phosphorus load was 20.48 t in total, with 68.1% from the upper part, and 31.9% from the lower part. The contributions of pollutant loads varied with different sources. For the entire watershed, the contributions to NH_4-N ranked as animal feedlots (62.5%), crop production (17.6%), rural households (17.6%), industry (16.0%) and soil erosion (0.8%), respectively. For TP loads, crop production and soil erosion were the two largest contributors that accounted for 42.0% and 35.6% of the annual total amount, followed by animal feedlots, rural household and industry with contributions at 20.1%, 2.1% and 0.2%, respectively. Thus it can be seen that industrial effluent had a minor effect on both NH_4-N and TP loads in whether upper or lower parts; while animal feedlots, crop production and soil erosion (for TP only) were major pollution sources that became the primary controlled targets of water environment governance in the study region.

Table 2. Pollutant load emission of NH_4-N and total phosphorus (TP) in the upper and lower parts.

Pollutant Load (t/year)		Industry	Rural Household	Animal Feedlots	Crop Production	Soil Erosion	Annual Total
Upper part	NH_4-N	0.40	2.93	17.12	2.93	0.21	23.59
	TP	0.02	0.23	3.42	4.57	5.70	13.94
Lower part	NH_4-N	0.59	2.34	3.47	2.87	0.06	9.33
	TP	0.03	0.19	0.69	4.04	1.59	6.54

3.2. Water Quality Simulation

To further investigate the impacts of terrestrial pollutant emissions on river water quality, the QUAL2K model was coupled to simulate the transformation and migration of pollutants in the main river. Taking the pollution load estimated from the export coefficient model (Section 3.1) as inputs, the model was calibrated to the measured concentrations of NH_4-N and TP at two sections of Yangjia and Denghua (Figure 1). The main calibrated parameters were hydrolysis coefficient (K_{hn}) and settling rate (V_{on}) of organic nitrogen, ammonium nitrification rate (K_{na}), and hydrolysis coefficient (K_{hp}) and settling rate (V_{op}) of organic phosphorus. Given a suitable range of each parameter determined from literatures [20,48], the parameters were adjusted through trial and error until the fitting results were satisfactory; other parameters except the above were set as the default values in the model. Calibrated parameter values of upper and lower parts were presented in Table 3.

Table 3. Calibrated parameter values and their suitable ranges for the QUAL2K model.

Parameters	Calibrated Values		Unit	Symbol	Range
	Upper Part	Lower Part			
Organic-N hydrolysis	0.30	0.25	day^{-1}	K_{hn}	0–5
Organic-N settling velocity	0.29	0.21	m/day	V_{on}	0–2
Ammonium nitrification rate	0.28	0.22	day^{-1}	K_{na}	0–10
Organic-P hydrolysis	0.45	0.42	day^{-1}	K_{hp}	0–5
Organic-P settling velocity	0.30	0.31	m/day	V_{op}	0–2

Figure 3 plotted the simulated and measured concentrations of NH_4-N and TP, as well as the corresponding evaluation statistic of R^2. The simulated results generally agreed satisfactorily with the measured ones, with R^2 above 0.8 for both NH_4-N and TP at the two sections. According to the criteria suggested by Moriasi et al. [49], the R^2 higher than 0.5 is considered acceptable, suggesting that the QUAL2K model was capable of simulating the transportation and migration of NH_4-N and TP in the Dengsha River.

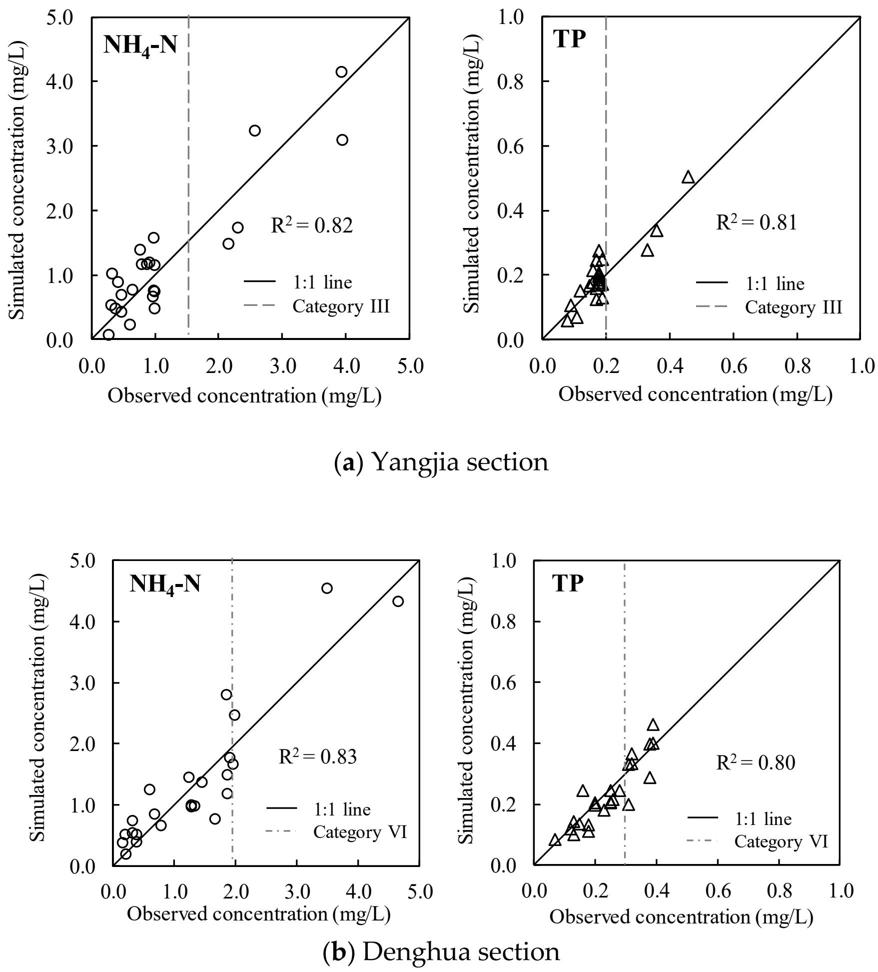
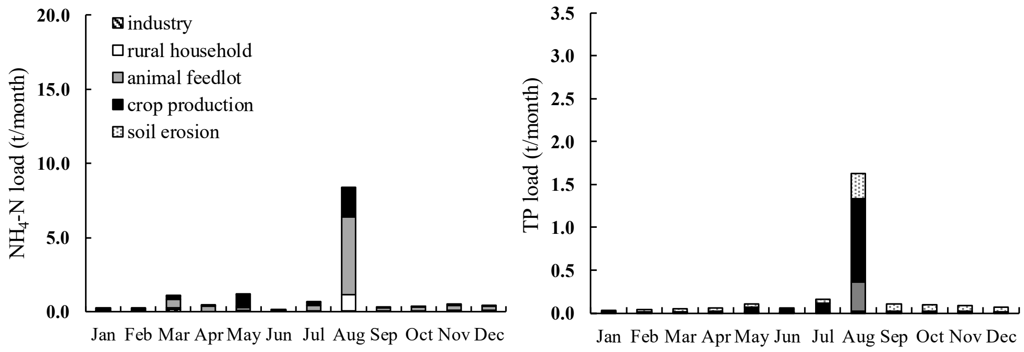


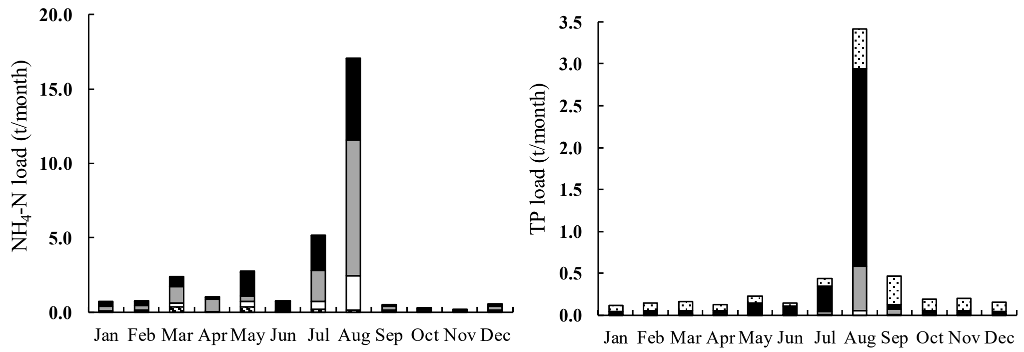
Figure 3. Measured and simulated monthly concentrations of NH_4-N and TP for the period 2014–2015 at (**a**) Yangjia and (**b**) Denghua sections. The corresponding coefficient of determination (R^2) for each figure is also indicated.

3.3. Spatiotemporal Analysis and Source Attribution of Pollutant Load

With the diversity and complexity of terrestrial sources in the study region, the spatiotemporal pattern of pollutant loads and the contribution from various pollution sources were analyzed to identify the major sources, and thus to provide scientific base for water quality governance. Average monthly NH_4-N and TP loads over the period of 2014–2015 at Yangjia (middle-stream) and Denghua (downstream) sections from each source are shown in Figure 4.



(**a**) Yangjia section



(**b**) Denghua section

Figure 4. Average monthly NH_4-N and TP loads over the period of 2014–2015 from various pollution sources at (**a**) Yangjia and (**b**) Denghua sections.

Pollutant loads of Denghua were higher than that of Yangjia. For the annual NH_4-N load, animal feedlot was the major contributor accounting for 60.5% and 48.3% at the middle and downstream sections, respectively. Crop production ranked the second with contributions of 22.5% to the middle section and 33.9% to the downstream section. Rural household ranked as the third largest contributor, accounting for 12.0% and 12.4% at the middle and downstream sections. Industries and soil erosion contributed the remaining 5.2% of the annual NH_4-N load. For the annual TP load, the majority was contributed by crop production, accounting for 50.2% and 55.4% at the middle and downstream sections, respectively. Soil erosion had a comparable contribution of TP load as crop production, which accounted for 31.2% and 30.3% at the middle and downstream sections, respectively. Unlike the large contribution to NH_4-N load, animal feedlot became the third largest contributor to TP load, with 17.2% and 12.7% contributions at the middle and downstream sections, respectively. Rural household and industry were insignificant sources with a total contribution at less than 2% of the annual TP load.

The contribution of each pollution source was highly associated with its location and magnitude of input load. As the animal feedlot was mostly scattered in the upstream region, it occupied a larger contribution of loads at the Yangjia section (60.5% for NH_4-N and 17.2% for TP) compared with the Denghua section (48.3% for NH_4-N and 12.7% for TP). While the reverse was true for the industry and crop production. The load contributions from the rural household and soil erosion presented no remarkable difference at the two sections. The contribution of industrial wastewater to pollutant loads were relatively small throughout the year, because the local factories and enterprises were mainly foundry, garment and metallurgical industries, resulting in few inputs of NH_4-N and TP loads. Non-point pollution sources were the main contributors responsible for river water deterioration for a number of reasons. One is for the hundreds of animal feedlots in the study area with their livestock manure mostly stacked in place. On the other, cropland takes up about 70% of the total basin area, and moreover, the intensity of fertilizer application in the study region is far above the criteria of ecological city with fertilizer use in China. Thus to reduce and control the pollutant loads from animal feedlot and cropland is the key to water contamination treatment and remediation.

The contribution of loads from each pollution sources exhibited intra-annual variations. Load from industrial source had no obvious change throughout the year, with the monthly load ranging from 0.02 t to 0.35 t for NH_4-N, and 0.00 t to 0.01 t for TP. This was due to the relatively steady discharge amount and low concentration of NH_4-N and TP of the industrial wastewater. Pollutant loads from non-point source pollution were larger during some months in spring, summer and autumn, i.e., March, May and July to September, while lower in winter. This can be explained with two considerations. On one hand, more water was consumed and more pollutants were generated during these month. There was higher water consumption in domestic use primarily for shower, washing and drinking. For animal feedlots, more sweeping water was consumed for cooling and insects-repelling purposes; as data indicated from the Statistical Report of Bureau of Environmental Protection of the Jinzhou New District, the discharge of animal wastewater in the study area was 30% higher in summer than in winter. The majority of pollutants from cropland occurred during May to August due to the fertilizer application in May and top dressing afterwards. On the other hand, since the effect of precipitation had been taken into account for estimating the pollutant loads that discharged into the river, the melting water in early spring and flood in summer (particularly for August) had led to relatively higher contribution from the non-point source pollution; while the reverse was true during October to next February when there was less rainfall and runoff (Figure 5).

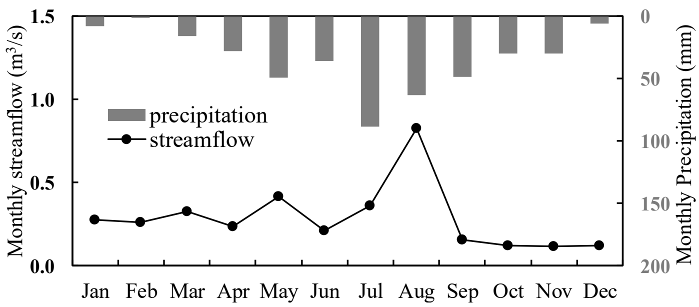


Figure 5. Average monthly observed precipitation at the meteorological station, and streamflow at the Yangjia hydrological station during 2014–2015.

4. Discussion

The monthly measured NH_4-N and TP concentrations were compared with the prescribed Category III (for Yangjia) and Category IV (for Denghua) standards, respectively, of the Chinese Surface Water Quality Standard (GB 3838-2002) [27], as shown in Figure 3. During the study period from 2014 to 2015, 29% of the NH_4-N measurements and 27% of the TP measurements have exceeded their permissible limits.

To achieve the target of water quality, the assimilative capacity of the river should remain sufficient. For this, the waste assimilation capacity (WAC), aiming at satisfying the water quality standard at the Denghua section, was calculated for each month based on the established QUAL2K model and the trial and error method. The monthly flow rate under a 75% exceedance probability was adopted, which represents a severe pollutant emission condition under a relatively low flow condition. As shown in Figure 6, the WAC, as expected, was relatively larger for March, April and July to September due to the higher stream flow. By comparing the WAC with pollution emission for each month, it could be found that the NH_4-N and TP emissions in 7 months of the year exceeded the corresponding WAC. Though there was still surplus capacity for several months to accommodate more pollution load, the WAC of the study region was overall overloaded. The analysis of WAC is an effective measure for policy makers to set sustainable goals for total loads control. More importantly, it proved that there was a strong need for implementing the integrated water quality governance plan in the study region.

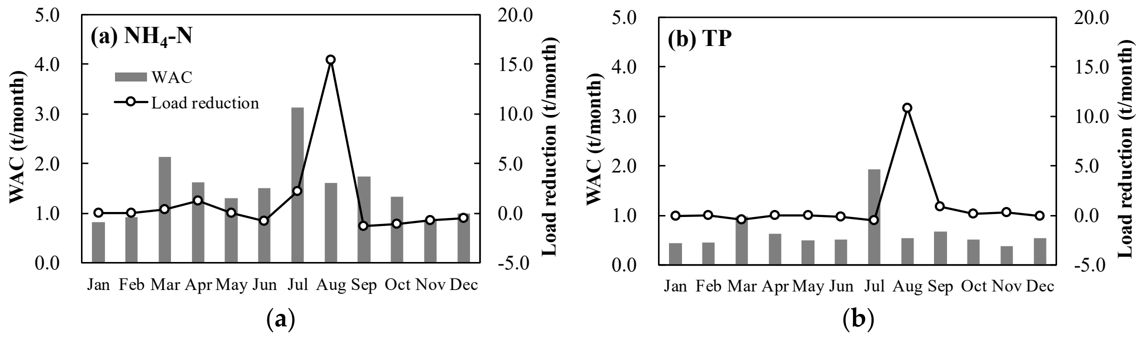


Figure 6. Waste assimilation capacity (WAC) to satisfy the water quality criteria at Denghua, and load reduction for each month for (**a**) NH_4-N and (**b**) TP. Load reduction is the difference between monthly pollution load emission and corresponding WAC; negative values indicate a surplus of capacity to accommodate more pollution load, and positive values indicate an overload of emission that should be reduced.

Results in this study indicated larger contributions of pollutant loads from crop production and animal feedlot, suggesting an imminent focus of pollutant control on these sources. The excessive application of livestock manure and fertilizer on agricultural fields were reported to lead to a nutrient over-enrichment, which were regarded as the largest sources of impairment of rivers, streams, lakes and reservoirs [50,51]. The major issue about crop production in this study was the excessive fertilizer application, which was up to 450 kg/ha per year and is far beyond the safety standard (225 kg/ha) of developed countries to prevent water pollution [52]. Lacking of scientific knowledge on fertilizers and guidance from agricultural extension services, the excessive fertilization is actually occurring in many regions of China [53,54]. Promoting better fertilizer application practices thus should be put in the top priority to reduce pollutant loads from agriculture, such as soil testing, precise fertilization, organic fertilizers promotion and water saving irrigation [55].

Animal feedlot was another potential source for the load reduction in the watershed. There should firstly be a clear division of the banned and confined regions for animal feeding. On this basis, the small-scale and centralized wastewater treatment systems should be equipped to the scattered and concentrated animal feedlots. In the meantime, to introduce technologies that can convert animal manure to biogas and organic fertilizers is an effective way, which could not only reduce the pollutant loads but also serve for organic fertilizer for agricultural land.

Soil erosion was found to be the second largest contributor of TP load in the study region. Actually, numerous efforts have been made for soil and water conservation, and thus for water pollution control in China and all over the world [56]. The vegetation restoration (e.g., converting the agricultural land to grassland and forest), as well as other agricultural conservation measures (e.g., crop rotation, strip cropping, surface mulching, minimum tillage and no-tillage), can be efficient to control the adsorbed pollutants in such an agriculture-dominated region [57]. In addition, engineering measures, such as terracing and silt check dams, can take effect quickly in retaining the water and sediment; however, disputes have arisen as these measures could interfere with the ecological functionality and stability [58].

As for the rural household sewage, although the contribution of which was not comparable to that of crop production and animal feedlot in the study region, it has been reported to be the dominant pollution source in many other watersheds, such as the Tai Lake [33] and the Yangtze River Basin in China [30]. The sewage collection system, as well as the wastewater treatment system are thus essential in these regions. Although this study indicated an insignificant impact on NH_4-N and TP loads from industrial activity, it could not be neglected since the other categories of contamination, e.g., heavy metal, benzene and oil, were not considered in this study; thus more emphasis should be paid to the monitoring and evaluation of these indexes to effectively control the industrial pollution on water quality.

In addition to the above discussed countermeasures, payments for ecosystem service (PES) has been widely promoted as an effective solution for sustaining the ecosystem service [59]. PESs are financial incentives (e.g., cash, kind, policy support and taxation reform) given directly to landholders to compensate them for implementing good land management; such compensation encourages them to "voluntarily" provide such services, instead of monetizing their "natural capital". The scheme has been implemented successfully in many regions of the world, including Asia, Europe, Latin America and Africa. In China, the "eco-compensation mechanism", an equivalent term of PES, has been widely implemented, with most of the programs targeting at improving water quality and quantity, controlling soil erosion and promoting eco-agriculture [59,60].

The analysis and countermeasures in this study could be an insightful example of other rural areas in China, where they are mainly characterized by diverse and complex pollution sources, weak water treatment facilities and a low level of environmental regulation. In addition, there are limitations in this study that could be further considered. One was that only the dry years of 2014 and 2015 were analyzed; thus further analysis covering different hydrological years is expected. The other was that the pollutant loads discharged into the river were estimated by the empirical export coefficients, which could be considered in further study using a watershed scale process-based model.

5. Conclusions

Water quality deterioration has prevalently occurred worldwide, especially in the rural areas in China. Countermeasures and precautions for water pollution should be fundamentally based on a comprehensive understanding of the sources of pollution and their relative contribution to the water quality deterioration. This study adopted a coupled approach of the empirical export coefficient model and the process-based river water quality model to estimate the NH_4-N and TP loads from various pollution sources and to quantify their contributions to the pollutant load in the Dengsha River of Dalian, China.

Results of the attribution analysis indicated that animal feedlot was the dominant source of NH_4-N pollution, followed by crop production, rural household, industry and soil erosion. While TP load from crop production was the largest, followed by soil erosion, animal feedlot, rural household and industry. The large number of animal feedlots and the overuse of fertilizers, aggravated by the weak water treatment ability and low water regulation level, were primary causes of the water pollution in the study region. The comparison between WAC and actual pollution emissions indicated that the WAC of the study region was overall overloaded. Further, suggestions for water pollution control and treatment regarding each source were proposed. This study highlighted the application of water quality models in water environmental management. Policy implications are the necessities of identifying the major pollution sources and understanding the overloaded or surplus capacity for pollutant loads, when formulating strategies and programs for water environment governance and management. This study could therefore be a reference example for similar polluted river basins in different parts of the world.

Author Contributions: Conceptualization, Z.X.; methodology, Z.X.; software, L.Y.; validation, L.Y.; formal analysis, Z.X. and L.Y.; writing—original draft preparation, Z.X.; writing—review and editing, L.Y.; supervision and funding acquisition, C.Z.

Funding: This research was funded by the National Natural Science Foundation of China (grant number 51809031), and the National Key Research and Development Program of China (grant number 2017YFC0406004).

Acknowledgments: Special thanks are given to the anonymous reviewers for their constructive comments that helped to greatly improve the manuscript.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Guo, H.; Liu, L.; Huang, G.; Fuller, G.; Zou, R.; Yin, Y. A system dynamics approach for regional environmental planning and management: A study for the Lake Erhai Basin. *J. Environ. Manag.* **2001**, *61*, 93–111. [CrossRef] [PubMed]
2. Zhang, P.; Liu, R.; Bao, Y.; Wang, J.; Yu, W. Uncertainty of SWAT model at different DEM resolutions in a large mountainous watershed. *Water Res.* **2014**, *53*, 132–144. [CrossRef] [PubMed]
3. Ouyang, Y. Evaluation of river water quality monitoring stations by principal component analysis. *Water Res.* **2005**, *39*, 2621–2635. [CrossRef] [PubMed]
4. Tian, Y.; Jiang, Y.; Liu, Q.; Dong, M.; Xu, D.; Liu, Y.; Xu, X. Using a water quality index to assess the water quality of the upper and middle streams of the Luanhe River, northern China. *Sci. Total Environ.* **2019**, *667*, 142–151. [CrossRef] [PubMed]
5. China Water Risk. New "Water Ten Plan" to Safeguard China's Waters. 2015. Available online: http://www.chinawaterrisk.org/notices/new-water-ten-plan-to-safeguard-chinas-waters/ (accessed on 5 October 2019).
6. Kampas, A.; Edwards, A.C.; Ferrier, R.C. Joint pollution control at a catchment scale: Compliance costs and policy implications. *J. Environ. Manag.* **2002**, *66*, 281–291. [CrossRef]
7. Edwards, A.C.; Withers, P.A. Policy measures to reduce phosphorus loss and site-specific environmental impacts. *IAHS Publ.* **2002**, *273*, 85–88.
8. Yang, X.; Liu, Q.; Fu, G.; He, Y.; Luo, X.; Zheng, Z. Spatiotemporal patterns and source attribution of nitrogen load in a river basin with complex pollution sources. *Water Res.* **2016**, *94*, 187–199. [CrossRef]
9. Chapra, S.C. Surface Water-Quality Modeling. 1997. Available online: https://www.researchgate.net/publication/48447645_Surface_Water-Quality_Modeling (accessed on 1 October 2019).
10. Gassman, P.W.; Sadeghi, A.M.; Srinivasan, R. Applications of the SWAT model special section: Overview and insights. *J. Environ. Qual.* **2014**, *43*, 1–8. [CrossRef]
11. Bouraoui, F.; Grizzetti, B. Modelling mitigation options to reduce diffuse nitrogen water pollution from agriculture. *Sci. Total Environ.* **2014**, *468–469*, 1267–1277. [CrossRef]
12. Devi, G.; Ganasri, B.; Dwarakish, G. A review on hydrological models. *Aquat. Procedia* **2015**, *4*, 1001–1007. [CrossRef]
13. Cox, B. A review of currently available in-stream water-quality models and their applicability for simulating dissolved oxygen in lowland rivers. *Sci. Total Environ.* **2003**, *314–316*, 335–377. [CrossRef]
14. Delkash, M.; Al-Faraj, F.A.M.; Scholz, M. Comparing the export coefficient approach with the soil and water assessment tool to predict phosphorous pollution: The Kan Watershed case study. *Water Air Soil Pollut.* **2014**, *225*, 60–69. [CrossRef]
15. Johnes, P.J. Evaluation and management of the impact of land use change on the nitrogen and phosphorus load delivered to surface waters: The export coefficient modelling approach. *J. Hydrol.* **1996**, *183*, 323–349. [CrossRef]
16. Grizzetti, B.; Bouraoui, F.; De Marsily, G. Assessing nitrogen pressures on European surface water. *Glob. Biogeochem. Cycl.* **2008**, *22*, GB4023. [CrossRef]
17. Behrendt, H.; Huber, P.; Kornmilch, M.; Opitz, D.; Schmoll, O.; Scholz, G.; Uebe, R. Nutrient Emissions into River Basins of Germany. Available online: https://www.umweltbundesamt.de/sites/default/files/medien/publikation/short/k1837.pdf (accessed on 1 October 2019).
18. Arnold, J.G.; Moriasi, D.N.; Gassman, P.W.; Abbaspour, K.C.; White, M.J.; Srinivasan, R.; Santhi, C.; Harmel, R.D.; Griensven, A.V.; Van Liew, M.W.; et al. SWAT: Model use, calibration, and validation. *Trans. ASABE* **2014**, *55*, 1491–1508. [CrossRef]
19. Young, R.A.; Onstad, C.A.; Bosch, D.D.; Anderson, W.P. AGNPS: A nonpoint-source pollution model for evaluating agricultural watersheds. *J. Soil Water Conserv.* **1989**, *44*, 168–173.
20. Chapra, S.C.; Pelletier, G.J.; Tao, H. *QUAL2K: A Modeling Framework for Simulating River and Stream Water Quality, Version 2.12: Documentation and Users Manual*; Civil and Environmental Engineering Dept., Tufts University: Medford, MA, USA, 2012.
21. Cho, H.J.; Ha, S.R. Parameter optimization of the QUAL2K model for a multiple-reach river using an influence coefficient algorithm. *Sci. Total Environ.* **2010**, *408*, 1985–1991. [CrossRef]

22. Fan, C.; Ko, C.H.; Wang, W.S. An innovative modeling approach using QUAL2K and HEC-RAS integration to assess the impact of tidal effect on river water quality simulation. *J. Environ. Manag.* **2009**, *90*, 1824–1832. [CrossRef]
23. Kannel, P.R.; Lee, S.; Lee, Y.S.; Kanel, S.R.; Pelletier, G.J. Application of automated QUAL2Kw for water quality modeling and management in the Bagmati river. *Nepal. Ecol. Model.* **2007**, *202*, 503–517. [CrossRef]
24. Park, S.S.; Lee, Y.S. A water quality modeling study of the Nakdong River, Korea. *Ecol. Model.* **2002**, *152*, 65–75. [CrossRef]
25. Rehana, S.; Mujumdar, P.P. River water quality response under hypothetical climate change scenarios in Tunga-Bhadra river, India. *Hydrol. Process.* **2011**, *25*, 3373–3386. [CrossRef]
26. Zhang, R.; Qian, X.; Li, H.; Yuan, X.; Ye, R. Selection of optimal river water quality improvement programs using QUAL2K: A case study of Taihu Lake Basin, China. *Sci. Total Environ.* **2012**, *431*, 278–285. [CrossRef] [PubMed]
27. State Environmental Protection Administration of the China (SEPA). *Environmental Quality Standards for Surface Water (GB3838-2002)*; China Environmental Science Press: Beijing, China, 2002.
28. Chinese Academy for Environmental Planning (CAEP). *Technical Guidelines of National Water Environmental Capacity*; CAEP: Beijing, China, 2003.
29. Ministry of Environmental Protection of the China (MEP); National Bureau of Statistics of the China (NBS); Ministry of Agriculture of the China (MOA). *The First National Survey of Pollution Sources Bulletin*; MEP, NBS, MOA: Beijing, China, 2010.
30. Wang, X.; Hao, F.; Cheng, H.; Yang, S.; Zhang, X.; Bu, Q. Estimating non-point source pollutant loads for the large-scale basin of the Yangtze River in China. *Environ. Earth Sci.* **2011**, *63*, 1079–1092. [CrossRef]
31. Shen, Z.; Chen, L.; Ding, X.; Hong, Q.; Liu, R. Long-term variation (1960–2003) and causal factors of non-point-source nitrogen and phosphorus in the upper reach of the Yangtze River. *J. Hazard. Mater.* **2013**, *252-253*, 45–56. [CrossRef]
32. 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]
33. Liu, B.; Liu, H.; Zhang, B.; Bi, J. Modeling nutrient release in the Tai Lake Basin of China: Source identification and policy implications. *Environ. Manag.* **2013**, *51*, 724–737. [CrossRef]
34. Renard, K.G.; Foster, G.R.; Weesies, G.A.; McCool, D.K.; Yoder, D.C. Predicting Soil Erosion by Water: A Guide to Conservation Planning with the Revised Universal Soil Loss Equation (RUSLE). 1997. Available online: https://www.ars.usda.gov/ARSUserFiles/64080530/RUSLE/AH_703.pdf (accessed on 1 October 2019).
35. Renard, K.G.; Yoder, D.C.; Lightle, D.T.; Dabney, S.M. Universal soil loss equation and revised universal soil loss equation. In *Morgan RPC, Nearing MA Handbook of Erosion Modelling*; Blackwell Publishing Ltd.: Cambridge, UK, 2011.
36. Didoné, E.J.; Minella, J.P.G.; Merten, G.H. Quantifying soil erosion and sediment yield in a catchment in southern Brazil and implications for land conservation. *J. Soil Sediment.* **2015**, *15*, 2334–2346. [CrossRef]
37. Gao, Y.; Zhang, Y.; Jiao, J.; Xie, Y. Sediment delivery ratios of typical watersheds on different spatial scales in Songhua River Basin and its affecting factors. *Sci. Soil Water Conserv.* **2016**, *14*, 21–27.
38. Guo, X.; Song, F.; Gao, Y.; Ma, F. Characteristics of lost sediment and its mutrient enriched effect on three types soil slope under simulated rainfall. *J. Soil Water Conserv.* **2014**, *28*, 23–28.
39. Wiscjmeier, W.H.; Smith, D.D. *Predicting Rainfall Erosion Losses: A Guide to Conservation Planning*; US Department of Agriculture: Washington, DC, USA, 1978.
40. Wischmeier, W.H. A soil erodibility nomograph for farmland and construction sites. *J. Soil Water Conserv.* **1971**, *26*, 189–193.
41. Liu, B.; Bi, X.; Fu, S. *Soil Loss Model for Beijing*; Science Press: Beijing, China, 2010.
42. Cai, C.; Ding, S.; Shi, Z.; Huang, L.; Zhang, G. Study of applying USLE and geographical information system IDRISI to predict soil erosion in small watershed. *J. Soil Water Conserv.* **2000**, *14*, 19–24.
43. Chen, L.; Xie, G.; Zhang, C. Spatial distribution characteristics of soil erosion in Lancang River Basin. *Res. Sci.* **2012**, *34*, 1240–1247.
44. Chen, D.; Lu, J.; Huang, H.; Liu, M.; Gong, D.; Chen, J. Stream nitrogen sources apportionment and pollution control scheme development in and agricultural watershed in Eastern China. *Environ. Manag.* **2013**, *52*, 450–466. [CrossRef] [PubMed]

45. Lindgren, G.A.; Wrede, S.; Seibert, J.; Wallin, M. Nitrogen source apportment modeling and the effect of land-use class related runoff contributions. *Hydrol. Res.* **2007**, *38*, 317–331. [CrossRef]
46. Leopold, L.B.; Maddock, T. The hydraulic geometry channels and some physiographic implications. In *Geological Survey Professional Paper 252*; US Government Printing Office: Washington, DC, USA, 1953.
47. Krause, P.; Boyle, D.P.; Bäse, F. Comparison of different efficiency criteria for hydrological model assessment. *Adv. Geosci.* **2005**, *5*, 89–97. [CrossRef]
48. US Environmental Protection Agency (USEPA). *Rates, Constants and Kinetics Formulations in Surface Water Quality*, 2nd ed.; EPA 600/3-85-040; USEPA: Athens, GA, USA, 1985.
49. Moriasi, D.N.; Arnold, J.G.; Van Liew, M.W.; Bingner, R.L.; Harmel, R.D.; Veith, T.L. Model Evaluation Guidelines for Systematic Quantification of Accuracy in Watershed Simulations. *Trans. ASABE* **2007**, *50*, 885–900. [CrossRef]
50. Ciofalo, V.; Barton, N.; Kretz, K. Safety evaluation of aphytase, expressed in Schizosaccharomyces pombe, intended for use in animal feed. *Regul. Toxicol. Pharmacol.* **2003**, *37*, 286–292. [CrossRef]
51. Risal, A.; Parajuli, P.B. Quantification and simulation of nutrient sources at watershed scale in Mississippi. *Sci. Total Environ.* **2019**, *670*, 633–643. [CrossRef]
52. China Council for International Cooperation on Environment and Development (CCICED). *Special Policy Study: Environmental Issues and Countermeasures Facing New Rural Development in China*; CCICED: Beijing, China, 2006.
53. Peng, S.B.; Tang, Q.Y.; Zou, Y.B. Current status and challenges of rice production in China. *Plant Prod. Sci.* **2009**, *12*, 3–8. [CrossRef]
54. Yang, X.; Fang, S. Practices, perceptions, and implications of fertilizer use in East-Central China. *Ambio* **2015**, *44*, 647–652. [CrossRef]
55. Wang, Y.; Zhu, Y.; Zhang, S.; Wang, Y. What could promote farmers to replace chemical fertilizers with organic fertilizers? *J. Clean. Prod.* **2018**, *199*, 882–890. [CrossRef]
56. Ran, L.; Lu, X.; Xu, J. Effects of vegetation restoration on soil conservation and sediment loads in China: A critical review. *Crit. Rev. Environ. Sci. Technol.* **2013**, *43*, 1384–1415. [CrossRef]
57. Hudson, N.W. *Soil and Water Conservation in Semi-Arid Areas*; FAO Soils Bulletin: Rome, Italy, 1987.
58. Chen, L.; Huang, Z.; Gong, J.; Fu, B.; Huang, Y. The effect of land cover/vegetation on soil water dynamic in the hilly area of the loess plateau, China. *Catena* **2007**, *70*, 200–208. [CrossRef]
59. Capodaglio, A.G.; Callegari, A. Can payment for ecosystem services schemes be an alternative solution to achieve sustainable environmental development? A critical comparison of implementation between Europe and China. *Resources* **2018**, *7*, 40. [CrossRef]
60. Zhen, L.; Zhang, H. Payment for Ecosystem Services in China: An Overview. 2011. Available online: http://lrlr.landscapeonline.de/Articles/lrlr-2011-2/download/lrlr-2011-2BW.pdf (accessed on 24 October 2019).