Environmental Science & Technology

Article

pubs.acs.org/est

Sources and Pathways of Nutrients in the Semi-Arid Region of Beijing–Tianjin, China

Benoît Pernet-Coudrier,[†] Weixiao Qi,[‡] Huijuan Liu,[‡] Beat Müller,[§] and Michael Berg[†,*]

[†]Eawag, Swiss Federal Institute of Aquatic Science and Technology, 8600 Dübendorf, Switzerland

[‡]State Key Laboratory of Environmental Aquatic Chemistry, Research Center for Eco- Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, People's Republic of China

[§]Eawag, Swiss Federal Institute of Aquatic Science and Technology, 6047 Kastanienbaum, Switzerland

Ⓢ *Supporting Information*

ABSTRACT: Semiarid regions worldwide are particularly prone to eutrophication, which causes immense ecological and economic problems. One region that is in transition and requires systematic research for effective intervention is the dry landscape of Beijing-Tianjin (P. R. China). We investigated the sources and spatiotemporal loads of nitrogen and phosphorus species over a one-year period in the Haihe catchment that drains the megacity of Beijing. Although wastewater treatment was improved in recent years, the rivers were heavily contaminated by 0.3–5.3 mgP L^{-1} and 3.0–49 mgN L^{-1}, with toxic levels of nitrite (≥1 $mgNO_2$–N L^{-1}) and ammonia (≥0.6 $mgNH_3$–N L^{-1}). The average NH_4^+ (16.9 mgN L^{-1}) increased by 160% compared to 1996-levels. Mass fluxes and $\delta^{15}N$-signatures revealed that nutrients originated almost exclusively from sewage. Furthermore, the water balance demonstrated that >90% of the polluted river water was diverted for irrigation, thereby threatening food safety and groundwater quality. Per capita loads of 1.42 kgN/yr and 115 gP/yr were comparable to the peak discharges typical of Europe and the United States in 1970–1990, but concentrations were 2–3 times higher in the Beijing–Tianjin region. Our research identified sewage as the predominant nutrient source in this semiarid region, which suggests that state-of-the-art wastewater treatment would drastically mitigate eutrophication and even more rapidly than was previously observed in Europe.

■ INTRODUCTION

Eutrophication of surface waters has become one of the most severe environmental problems in developing and transitioning countries. This issue is particularly pronounced in arid and semiarid regions of Asia and sub-Saharan Africa,[1,2] where populations are constantly increasing. The consequences are oxygen depletion in rivers, fish kills, algal blooms, siltation of water bodies, and increases in drinking water treatment costs.

In the western world, research on the mitigation of eutrophication conducted from the 1970 to the 1990s, and intervention strategies derived thereof, have triggered a marked improvement in the aquatic environment. A similar approach is now needed in the transitioning regions. Here, the situation differs from the former eutrophication problems of the West, as booming cities are situated next to poor rural areas and cause different patterns of nutrient contamination than what were experienced in Europe or North America. Northern China, which has several megacities in dry landscapes, is particularly suitable for initiating these types of efforts, because serious eutrophication problems are more than evident, and funds for mitigation are more readily available than in other nations.

Within only two decades, China has evolved into one of the largest economies, with a GDP growth rate of nearly 10%.[3] However, awareness of environmental degradation and the corresponding legislation and investment lag behind the present speed of increasing productivity, which has consequences of rapid urbanization, high demand of resources including energy and water, and the subsequent pollution of air, water, and soil.[3–6] This development is primarily felt in the centers along the coast and in the megacities of Northern China.

The Beijing–Tianjin region has the highest growth rates in economy and population and therefore faces increasingly severe water scarcity. In 2007, the Beijing water availability dropped to 230 $m^3\ y^{-1}\ inh^{-1}$, which is only 2.7% of the 8500 $m^3\ y^{-1}\ inh^{-1}$ world average.[7,8] Many rivers ran dry,[9,10] partly due to 25 years of drought recorded since the 1970s, but also due to extensive water consumption of the growing population and industry, and to intensified farming that relies largely on irrigation.[7–9,11] In addition, nutrient concentrations (N and P) in the Haihe river system have massively increased in the past 40 years,[8,12] mostly because of draining of untreated sewage from the megacities[8,13] and possibly the overuse of chemical fertilizers.[14]

Received: August 25, 2011
Revised: February 19, 2012
Accepted: February 22, 2012
Published: March 8, 2012

About 30% of China's wheat and 20% of its corn are produced in the agricultural area between Beijing and Tianjin.[15] The consequences are grave deterioration of water bodies and shifts in marine algal communities due to the altered Si:N:P ratio.[16,17] Some areas of the Chinese coastal waters are listed among the largest dead zones of the world,[18] and harmful algal blooms are becoming increasingly more serious.[19,20] Nine new wastewater treatment plants (WWTPs) were installed before the 2008 Olympic Games with the aim of treating 90% of the Beijing wastewater, but their effectiveness has so far not been evaluated.

The goal of our research was to establish an overarching budget of nutrient fluxes in the main waterways of the Beijing-Tianjin region—a task that has seldom been carried out to date in any of the rapidly developing centers of Asia and Africa. We assessed the spatial and temporal patterns and loads of nitrogen and phosphorus species from the Shahe reservoir upstream of Beijing to the Bohai Bay at Tianjin, with the aim of providing a basis for appropriate mitigation strategies in these semiarid regions.

MATERIALS AND METHODS

Hydrology. The Shahe reservoir upstream of Beijing is a shallow 1.8 km^2 lake from where the Wenyu River (called North Canal further downstream) runs for 240 km to the Bohai Bay (Figure 1). On its way, this river grows from a trickle of ~1 m^3/s at site 1 to a 150-m-wide canal at site 13. It receives a large fraction of the Beijing WWTP effluents by way of four tributaries: the Qing River (between sites 3 and 4, Figure 1), the Beixiao River (between sites 4 and 5), the Tonghui River (between sites 5 and 6), and the Liangshui River (between sites 6 and 7). In the upper reaches (between sites 2 and 4), untreated wastewater is discharged into the river from numerous small open sewers. Two major canals divert water from the North Canal for irrigation to the agricultural area between Beijing and Tianjin, i.e., to the Chaobaixin River (between 5 and 6) and the Qinglongwan River (between 8 and 9). Gauge readings for daily river water discharge at sites 1, 5, 9, and 13 were acquired from the central hydrology station of Beijing and the Bureau of Hydrology and Water Resources Survey of Langfang, Hebei Province. Data of daily loads of treated wastewater discharged by the nine Beijing WWTPs were obtained from the facility managers. Wastewater from Tianjin is discharged chiefly to the Yongdingxin River, between sites 13–16, i.e., downstream from the last dam in the catchment (Figure 1). This final river section is brackish and tidal, which prevents quantification of riverine water discharge.

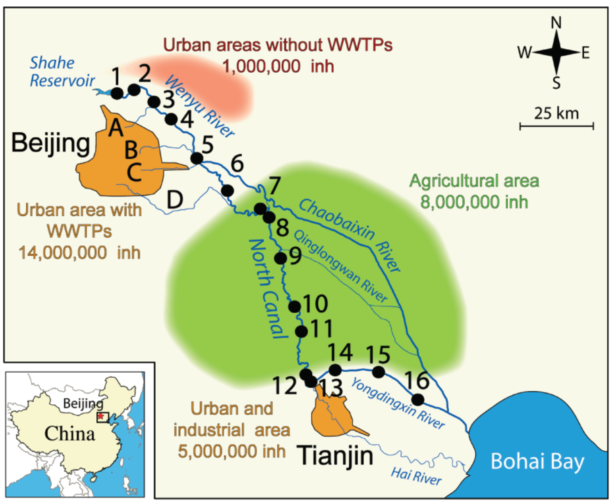

Figure 1. Haihe river system, land use, and population in the Beijing–Tianjin region, China. The numbers depict our sites of investigation [corresponding geo-positions are provided in Table SI-1 of the Supporting Information (SI)]. Letters A–D denote tributaries draining the wastewater effluents of Beijing, i.e.: A: Qing River; B: Beixiao River; C: Tonghui River; and D: Liangshui River. Note that Beijing had a total population of some 20 million in 2010, from which wastewater of 14 million was discharged into the studied river system.

Sampling Sites, Water Analyses, and Budgets. To gain a first overview on the occurrence and abundance of nutrient species, river water was collected along the 240-km river section at 16 selected study sites (Figure 1) in the dry season in April 2009 as well as in the wet season in July 2009. On the basis of this initial assessment, key sites 1, 5, 9, 12, and 13 were then monitored monthly from July 2009 to June 2010. Weekly and diurnal variations were investigated with daily samples (collected at the same hour from July 20–27, 2009) and hourly samples (July 23–24, 2009), respectively, at sites 1, 5, 9, 12, and 13. The four tributaries Qing, Beixiao, Tonghui, and Liangshui, which drain the wastewaters from Beijing, were also investigated. Effluents from the five largest Beijing WWTPs (Qinghe, Jiuxianqiao, Beixiaohe, Gaobeidian, and Xiaohongmen) were sampled in May 2009, December 2010, and March 2011 (24 h-composite samples) to assess per-capita nutrient loads from Beijing.

Water was collected by scooping river water with a bucket from a bridge or a dam. Temperature, pH, and dissolved oxygen (DO) were measured in the field, whereas DO measurements were verified with spectrophotometric Winkler titrations.[21] Details of sample preparation and chemical analyses are described in the Supporting Information (SI) for alkalinity, total suspended solids, water isotopes, as well as for N and P speciation, that is total phosphorus (TP),[23] particulate phosphorus (PP), total dissolved phosphorus (TDP), dissolved inorganic phosphorus (DIP), dissolved organic phosphorus (DOP), total nitrogen (TN), total dissolved nitrogen (TDN), particulate nitrogen (PN), NO_2^-, NO_3^-, and NH_4^+ (sum of NH_3 and NH_4^+), and dissolved organic nitrogen (DON). Calculations of loads and budgets of water and nutrients are also detailed in the SI, together with estimated errors.

RESULTS AND DISCUSSION

River Discharge and Water Budget. No periodicity (daily, weekly or seasonally) in river water discharge was observed. The occasional operation of river dams caused intermittent fluctuations in flow, but no systematic time patterns were noted. The water flow diagram established in this study (Figure 2) shows that Beijing discharges an annual average of 29.5 $m^3\ s^{-1}$ raw or treated wastewater into the Haihe river system. At a daily average consumption of 200 L inh^{-1},[22] this corresponds to about 14 million people, or 70% of Beijing's current population. The large contribution of wastewater to the river discharge was well reflected in the isotopic composition of river water (δ^2H and δ^{18}O), which mirrored the signatures of raw and treated wastewater as well as of groundwater used as supply water in Beijing (see Figure SI-1 of the SI).

About 480 mm yr^{-1} of rain fell in this semiarid landscape in 2009–2010, which is representative of the average of 450 mm yr^{-1} for the years 1999–2004.[23] Around 80% of the precipitation occurred between June and September, the warmest season with an average annual evaporation of ~1100

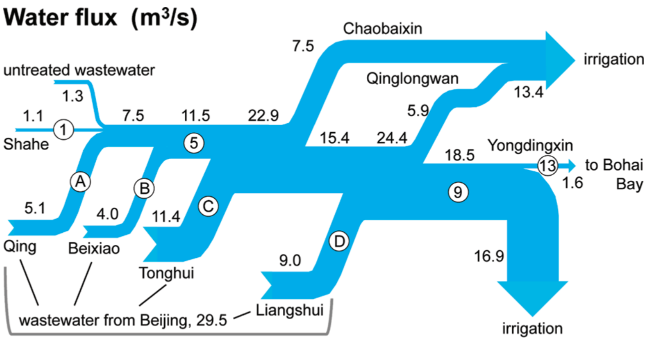

Figure 2. Flow diagram of water discharge in the Beijing region (Haihe river system). Encircled numbers and letters refer to the sites labeled in Figure 1. The discharge amounts for the Chaobaixin River and the Qinglongwan River do not account for additional tributaries along their way.

mm yr^{-1},[10] which is more than twice the average annual precipitation. Huang et al.[24] observed that rain events of up to 80 mm in rural areas (plain of the Haihe basin) did not produce surface runoff to rivers and channels, and events with >80 mm occurred only once in five years.[23] Another study found water runoff during heavy summer precipitation in some areas of Beijing City.[25] However, in agreement with our observations on water discharge and nutrient sources (see below), these reports concluded that rainwater runoff from agricultural soils was generally marginal.

Of the annual average of 18.5 m^3 s^{-1} of river water discharged below Beijing (site 9, Figure 2), a surprisingly small fraction of <10% (1.6 m^3 s^{-1}) actually Tianjin at site 13, and eventually the sea. Our investigation revealed that the missing 16.9 m^3 s^{-1} vanished from the river as a result of water withdrawal for irrigation. In fact, several dams along the river divert water to a network of irrigation channels from where countless farmers pump water to irrigate their crops. Similarly, the large amount of water channeled from downstream Beijing to the Chaobaixin and Qinglongwan rivers (13.4 m^3 s^{-1} on average) is also used to irrigate agricultural land. This raises concerns, since the river's water pollution status surpasses grade V of the national quality standard, which means that this water should not be used for any purpose.[26] In addition, groundwater from a 60−100 m depth is excessively pumped to supplement the demand for irrigation, despite the pronounced decline in groundwater levels (currently some 20 m) observed over the past three decades.[8,9,27]

Spatial Patterns of Nutrient Concentrations. In contrast to the commonly observed increase in pollutants in rivers passing urban and/or agricultural areas, the concentrations of TN and TP decreased significantly from the Shahe reservoir to Tianjin (sites 1−12, Figures 3). This was due to the very high nutrient concentrations in the upstream Shahe reservoir of up to 3.2 mgP L^{-1} DIP and 33 mgN L^{-1} NH_4^+. These nutrients originate largely from the discharge of untreated domestic sewage and/or sludge from animal husbandry, mainly poultry.[24] Downstream from the reservoir, between sites 1 and 4, countless small sewers release untreated sewage to the river, some of which discharge as little as 1 L s^{-1}.

Treated wastewater from 14 million inhabitants of Beijing (A−D in Figure 1) enters the river between sites 4 and 7. This water had lower nutrient levels, thereby diluting the river's N and P concentrations downstream. Only the Gaobeidian WWTP, which is the biggest facility of Beijing to date, with a

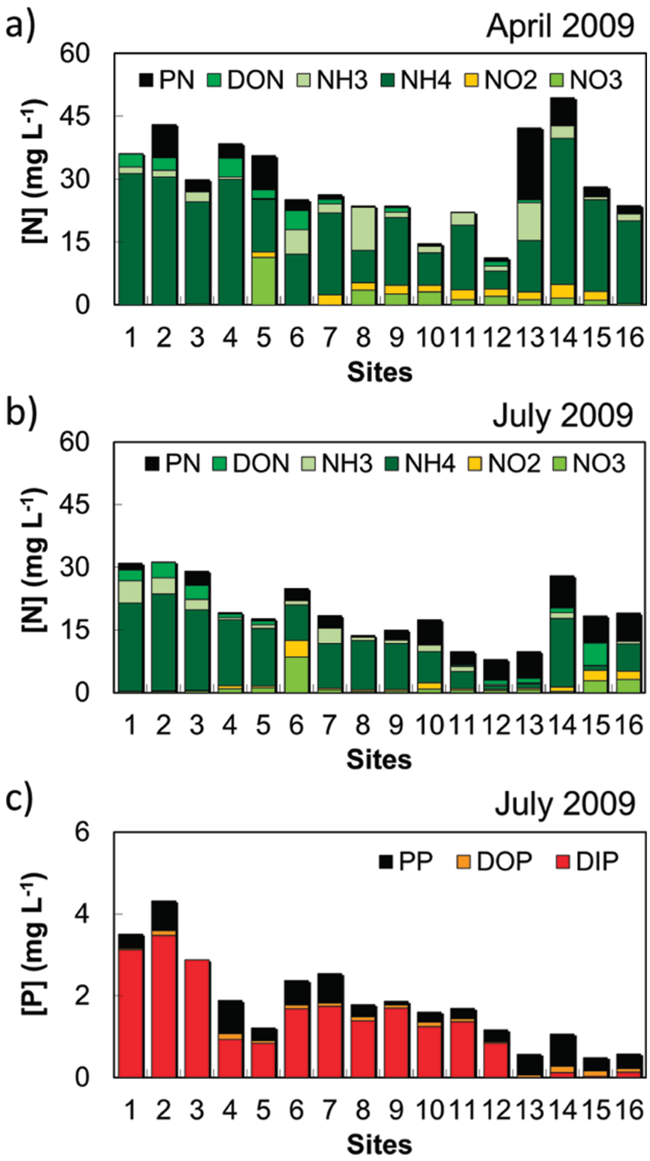

Figure 3. Spatial variations of N species (a and b) and P species (c) along the investigated 240 km of the Haihe river system in April and July 2009. P species in April 2009 (see Figure SI-2 of the SI) displayed the same trends as in July 2009. Note that the sampling sites are 5−25 km apart from each other.

hydraulic load of around 1 million m^3 d^{-1} (11.5 m^3 s^{-1}) of sewage discharged to the Tonghui River (downstream site 5), increased the concentration of TP again considerably at site 6 (Figure 3).

Below sites 13−16, the TN concentrations increased again to 30−50 mgN L^{-1} as a result of the draining of Tianjin wastewater into this final river section. This pattern was not observed for P, perhaps due to a better elimination of P by the Tianjin WWTPs, but most probably also as a result of adsorption onto suspended particles in this mixing zone of freshwater and seawater, which is reflected in PP being the dominant species (Figure 3).

Individual N species, plotted in Figures 4 and SI-3 of the SI, illustrate that the Tonghui River drains wastewater with the highest NO_3^- and NO_2^- levels (site 6), indicating only partial nitrification in the upstream WWTPs. Concentrations of almost 4 mgN L^{-1} NO_2^-, in combination with about 1 mg L^{-1} NH_3

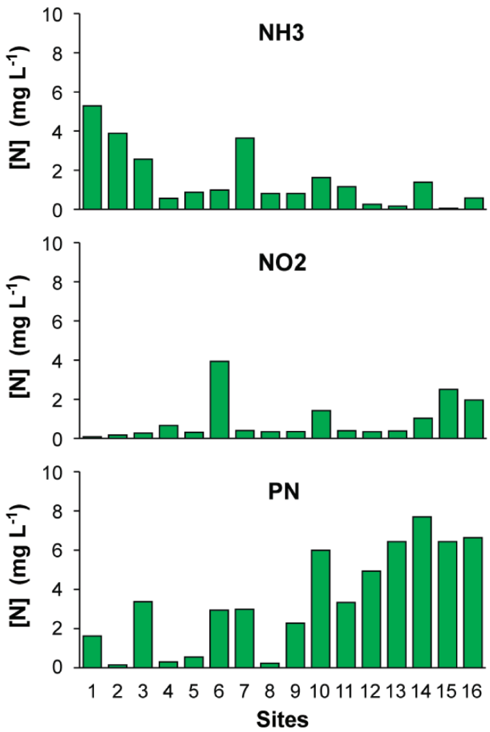

Figure 4. Spatial variations of NH_3, NO_2^-, and PN along the investigated 240 km of the Haihe river system in July 2009. The decrease in NH_3 and NH_4^+ (shown in Figure SI-3 of the SI), together with the increase of NO_2^- and NO_3^- (Figure SI-3 of the SI), point to partial nitrification. PN also increases due to assimilation by algae. Note that the sampling sites are 5–25 km apart from each other.

measured in July 2009 at site 6, are highly toxic[28] and may trigger the frequently observed fish kills. NH_3 concentrations between 0.1 and 10 mgN L^{-1} (87% ≥0.6 mgN L^{-1}) persisted throughout the year at all sites, with levels generally peaking at sites 1, 8, and 13, where pH values >9 were common (Figure 4). NO_2^- levels surpassed the acute toxicity level of 1 mgN L^{-1} in 46% of the samples.

At an average oxygen saturation of only 30% (0–75%) between sites 1 and 9, nitrification in the rivers is sluggish. Nevertheless, algal growth incorporates a substantial amount of dissolved nitrogen, particularly during the summer months. This process was reflected in increasing PN concentrations along the course of the river in July 2010 (Figures 4 and SI-3 of the SI), when abundant algae were visually more than evident at the sampling sites.

Sparse Temporal Variability of N and P. Whatever the site or the season, the quality of the river water was always worse than grade V (the lowest) of the Chinese national standard due to low oxygen (<2 mgO_2 L^{-1}), high total N (>2 mgN L^{-1}), and especially NH_4^+ (>2 mgN L^{-1}), and high P concentration (>0.4 mgP L^{-1}).

Diurnal Variation. The nutrient concentrations showed no diurnal pattern during the 24 h of observation (Figure 5f), although a heavy rain event occurred on the day of the investigation, with a magnitude of 90 mm in less than 2 h, which represents at least a decennial rain (Figure 5c). Neither the composition of major ions (see Table SI-2 of the SI) nor the water isotope signatures (Figure 5c) showed any evident influence of rain or runoff input. Hence, our data suggest that dilution of river water by rain was negligible even for the exceptionally intense rain event experienced here, an observation also reported by Huang et al.[24] The steep increase in water discharge (Figure 5c) is therefore more likely a result of upstream river-gate opening, performed as a precautionary measure to reduce the risk of flooding.

Weekly Variation. In analogy to the stagnant diurnal situation, variations in N and P concentrations were likewise marginal over the course of one week in July 2009 (Figure 5e), despite pronounced discharge fluctuations ranging from 6 to 33 m^3 s^{-1} (Figure 5b). However, the isotopic signature of water increased in the aftermath of the heavy rain event, reflecting a changing ratio of water sources in the catchment.

Annual Variation. A seasonality of TN, NO_3^-, and NO_2^- concentrations was evident only over the course of one year, with higher levels in winter and lower levels in spring and summer (Figure 5d). However, DIP and TP remained fairly constant over the seasons. Figure 5 shows temporal variations from site 9 only, but the same annual trends were observed at the other investigated sites (1, 5, 12, and 13; see Table SI-2 of the SI). The seasonal pattern of NO_3^- and NO_2^- likely reflected a varying efficiency of biological N-removal in the WWTPs (and in the river), with better performance during the warm seasons (i.e., March-September). This conclusion was corroborated by our three sampling campaigns conducted in May 2009, December 2010, and March 2011 at the five biggest Beijing WWTPs (see Materials and Methods section). These results displayed a large variability (over time and among the WWTPs) of the N-removal efficiency, at 16 to 93% (average: 66 ± 28%). Variable performance in seasonal nutrient removal was also reported in a recent study that investigated nutrient concentrations in Beijing's WWTPs over a 2 year span.[29]

The winter situation is characterized by temperatures between +10 and −10 °C, which lowers the biological activity of both the treatment plants and the biota in the river. Summers are very hot with temperatures up to 32 °C, which increases: (i) the efficiency of WWTP processes like nitrification/denitrification, (ii) volatilization of NH_3 due to alkaline conditions (pH 8–9) caused by photosynthesis and lower Henry coefficient, and (iii) biological uptake of N in the river. The phosphorus dynamics showed a slightly different picture, with less variation and smaller amplitude over the year, most probably due to P exchange between water, particles, and sediment; i.e., settling of PP and partial release of DIP in these anoxic river waters.

In summary, N and P concentrations did not correlate with water discharge, nor were seasonal patterns evident in any of the studied river sections (apart from N loads that were affected by the seasonally varying efficiency of WWTPs and the natural processes in the river such as NO_3^- uptake in the summer months, Figure 5d). Thus, these observations provide further evidence that wastewater is the major source of nutrients in the river. The main constituents of the TN and TP loads were NH_4^+ and DIP, representing 70% and 67% of the total loads (average on all sites over the 12 months of sampling). Ammonium is known to originate mainly from urine and feces of domestic and animal husbandry wastewater, whereas a significant fraction of P also stems from P-containing detergents, which are not yet banned in China and usually contain 1% P by weight.[30]

Loads of Nitrogen and Phosphorus. The nutrient budgets presented in Figure 6 are the first of this kind established for the Beijing–Tianjin region. The flow diagrams of nutrient loads reveal that Beijing and its suburbs discharged an annual average of 54.5 tN d^{-1} and 4.4 tP d^{-1} into the Haihe

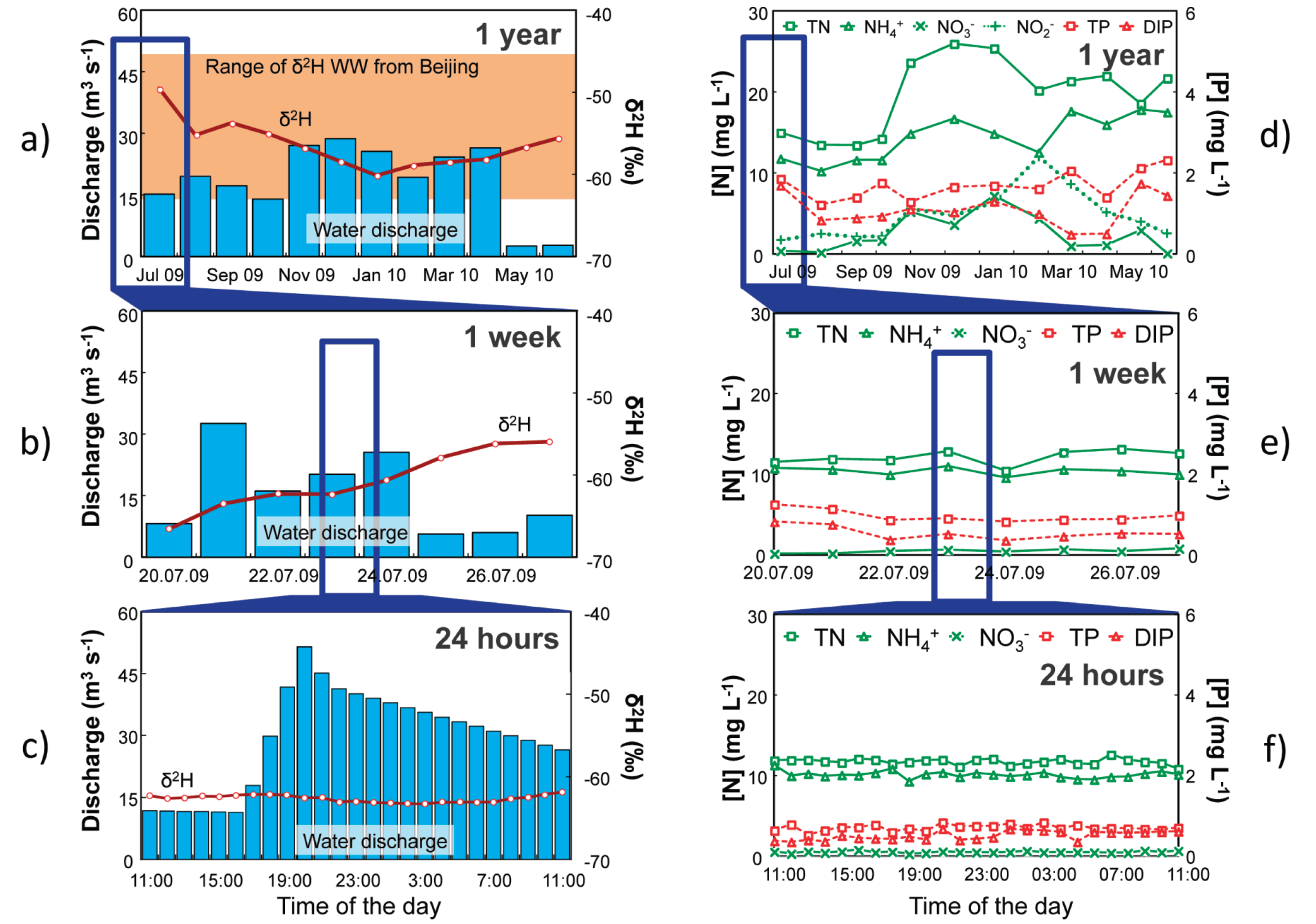

Figure 5. Temporal variability of water discharge, water isotope signatures (δ^2H), and concentrations of N and P species at site 9. (a) and (d), monthly measurements during one year (July 2009−June 2010). (b) and (e), daily measurements during one week (July 20−28, 2009). Parts (d) and (f) are hourly measurements during 24 h (July 23−24, 2009).

river system. The major source of both nutrients were wastewater effluents (>90%), with the Tonghui River carrying the effluents from the Gaobeidian WWTP contributing >50%. Raw sewage discharges upstream from the Shahe reservoir and in the Wenyu River were significant point sources of the upper subreach, causing high concentrations. However, loads were small and contributed only about 3% to the overall budget.

The nutrient flow diagrams presented in Figure 6 consist of independent measurements and are well balanced, which emphasizes our conclusion that sources other than wastewater, such as industrial input, agricultural nonpoint sources, and atmospheric deposition, were negligible. Moreover, δ^{15}N and δ^{18}O isotopic signatures of NO_3^- (Figure SI-4 of the SI) confirm that sewage was the dominant source of N in the river. Volatilization of NH_3 from the rivers was negligible, with an estimated 0.01−0.3 t d^{-1} between sites 1−12 (river surface area 20 km^2, average NH_3−N 1 mg L^{-1}, temperature 4−30 °C).[31]

A previous study[32] of 16 large river basins in China, including the Haihe, reported that agricultural fertilizer was the dominant source of DIN, while sewage was the major source for DIP between 1970 and 2000. The study predicted that these sources would still dominate in 2030 and 2050, whatever the chosen scenarios. However, for the first time in China, our study highlights the dominant contribution of sewage (treated or not) and the negligible contribution of agricultural activities not only for P but also for N loads in this river system. This important finding shows that (i) the share of wastewater borne nutrients could be generally underestimated in regions with similar water regimes as the Haihe River catchment, and (ii) there is a need to develop methodologies to reliably and comprehensively assess nutrient pathways and fluxes in other regions of China, preferably complemented by a permanent monitoring network.

On the basis of the nutrient loads of the rivers and the estimated 14 million inhabitants of the Beijing watershed, we assessed a production of 1420 gN y^{-1} inh^{-1} and 115 gP y^{-1} inh^{-1}, or 3.9 gN day^{-1} inh^{-1} and 0.32 gP day^{-1} inh^{-1}. This amount of N is close to the values reported for untreated wastewater around the globe (1650−1850 gN y^{-1} inh[−133,34]), whereas typical values for treated wastewater are considerably smaller (110−800 gN y^{-1} inh[−133,35]). The estimated P discharge rate, however, was within the global range published for treated effluents (91−211 gP y^{-1} inh^{-1}).[35,36] This observation reflects the higher treatment efficiency for P, which is partly removed by flocculation during treatment and by the settling of particles in the river. In contrast, sluggish nitrification/denitrification processes in the WWTPs hinder N removal. The city of Beijing is still rapidly growing, with an increasing number of households being connected to WWTPs. However, the treatment facilities, which were planned in 2002/2003 for the estimated number of inhabitants living in Beijing in 2008, are today often operating beyond their projected capacity as a result of the considerably larger population.

Wastewater from Tianjin spills into the Yongdingxin River and other channels that discharge directly to the sea. Assuming

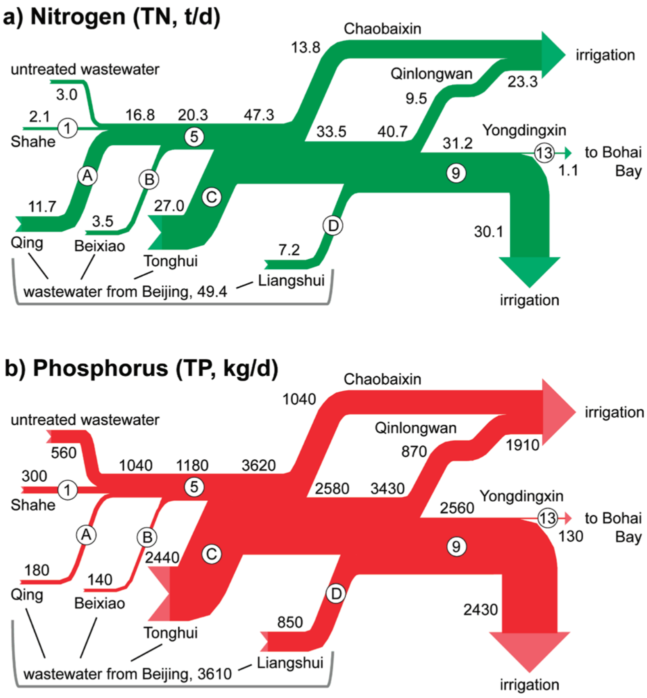

Figure 6. Flow diagrams of (a) daily loads of total nitrogen and (b) daily loads of total phosphorus in the Beijing region. All values are based on independent measurements. Loads of the Chaobaixin river and the Qinglongwan river do not account for additional tributaries and discharges along their way. Wastewater of Tianjin enters the river downstream of site 13, where tidal conditions prevent the measurement of riverine water discharge and thus nutrient fluxes to Bohai Bay. However, a rough estimation of nutrient loads discharged at Tianjin into the sea is provided in the text.

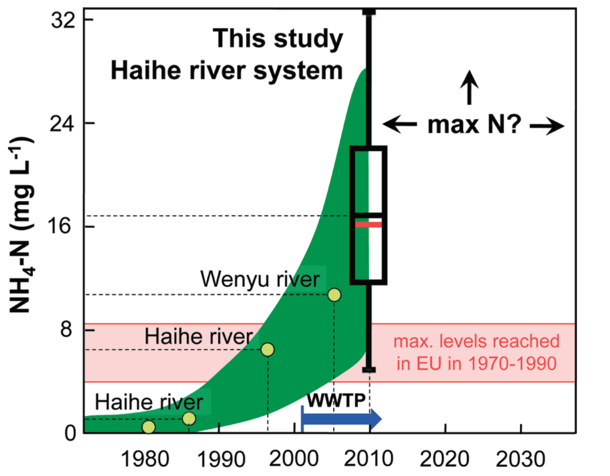

Figure 7. Temporal trends of average NH_4^+ concentrations in the Haihe watershed. The concentration range determined in our 12-month study period (2009–2010, box plot) demonstrate that nitrogen levels are still steeply increasing despite the new Beijing WWTPs that have been in operation since 2008. The green shading represents overall uncertainties involved in the past measurements (data from refs 10 and 37–39).

the same per capita production of N and P as determined for Beijing, the 5 million inhabitants of Tianjin release 19.2 tN day^{-1} and 1.6 tP day^{-1} into the Bohai Bay, thereby contributing significantly to the eutrophication of this part of the East China Sea.

Future Trends. Over the past few decades, concentrations of N and P species have increased sharply in the Haihe watershed (Figure 7). Despite the huge efforts spent, such as the construction of more than 4000 km of sewers and 9 new WWTPs to treat about 90% of the wastewaters of Beijing, these measures have had no apparent effect, as concentrations continue to increase exponentially.

When compared to N and P loads measured in other river systems of the world during their nutrient peak years in 1965–1970, such as in the Mississippi,[40] Seine and Scheldt,[41] and Rhine rivers,[42] the regional loads in the Haihe River system of 1330 kgN km^{-2} y^{-1} and 110 kgP km^{-2} y^{-1} today are quite similar. However, due to the semiarid climate and the much smaller water discharge, as well as the continuing drought, the concentrations of N and P species in the Haihe river system are 2–3 times higher than the maximum concentrations observed in the 1970s in Europe and the U.S.[43−45] From the 1950s to the 1990s, N and P fluxes in European rivers increased due to the combined effect of three causes: (i) intensification of agriculture involving the massive use of synthetic N and P fertilizers; (ii) introduction of polyphosphate-containing detergents that resulted in a three-to-4-fold increase in domestic P-release, and (iii) treatment of urban wastewater primarily aimed at the mineralization of organic matter, neglecting the elimination of N and P. The Beijing–Tianjin region currently displays all of these same features, and thus one could expect that peak levels of N and P may now be reached. If efficient mitigation measures were to be introduced, such as banning of P-detergents and inclusion of state-of-the-art wastewater treatment, then significant improvements in P to near-natural levels can be expected to be established over the following 30 years, according to the historical study of Billen and Garnier.[41]

Regarding N, the drastic increase was stopped in Europe and the U.S. in the 1980s, but 20–30 years later N fluxes are still far above pristine levels due to countless nonpoint sources that are difficult to control.[40,41] However, in the Beijing–Tianjin region, where the climate is dry and the N-sources are largely restricted to wastewater, installation of sufficient wastewater treatment facilities with state-of-the-art denitrification efficiency has a high potential to drastically cut down nutrient concentrations and mitigate eutrophication. Banning the use of P-detergents in China would certainly be an additional prerequisite to achieving this goal. In fact, with little nutrient input derived from agriculture and with wastewater effluents that are low in nutrient concentrations, the Haihe river system could recover from eutrophication even faster than has been observed in many regions in Europe and the U.S., where nutrient runoff from agriculture remains substantial. Similar situations to that seen in China are likely present in sub-Saharan Africa and in further semiarid regions of the world.

A key to success would be to build a well-designed monitoring network along the sewers and rivers that would enable the long-term documentation of changes in crucial water quality parameters and water quantity. The present study provides valuable grounding for the placement of monitoring sites. Besides adequate installations to collect water discharge-proportional samples and conserve them on-site, a dedicated analytical laboratory with well-trained personnel needs to be established. Finally, it has to be kept in mind that high N and P pollution from sewage is often accompanied by other harmful contaminants such as heavy metals, biocides, pharmaceuticals, and persistent organic pollutants.[46−49] As a consequence of fertilizer and wastewater seeping from the irrigated fields into the aquifers, groundwater contamination is already evident in several regions of northern China.[3,9,50,51] A successful mitigation strategy therefore includes long-term chemical monitoring programs for the rivers and groundwater resources, to assess the efficiency of intervention measures.[45] This would ideally tackle a representative set of both inorganic and organic pollutants in the aquatic environment.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Information regarding geopositions of the sampling sites, sample preparation and procedures of chemical analyses, database of chemical species quantified in river waters, plots of nutrient species variation along the river system, plot of water isotope signatures (δ^2H and δ^{18}O), and plot of δ^{15}N and δ^{18}O signatures of NO_3^- in Beijing wastewater and river water. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*Phone: +41-58-765 5078; e-mail: michael.berg@eawag.ch.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank Jiuhui Qu and Min Yang (RCEES) for their constant and generous support. Huachun Lan, Huimin Ren, Xiaobin Liu, Cui Li, Mingzhu Zhu, Xiaoli Du, Wenxin Gong, Xiaoyu Wu, Pengfei Xia, Meng Qiao, Caroline Stengel, and Ruth Stierli are acknowledged for their excellent assistance in sampling campaigns and instrumental analyses, and Guoying Bai, Yajuan Wang (Central Hydrology Station of Beijing), and Wenhao Chai (Bureau of Hydrology and Water Resource Survey of Langfang, Hebei Province) for providing discharge data. Yongjun Jiang and two anonymous reviewers provided valuable suggestions to the manuscript. This study was funded by the External Cooperation Program of the Chinese Academy of Sciences, Grant No. GJHZ0908, and by the Sino-Swiss Science and Technology Cooperation Program of the Swiss State Secretariat for Education and Research, project No. IZL CZ2 123912.

■ REFERENCES

(1) Vörösmarty, C. J.; McIntyre, P. B.; Gessner, M. O.; Dudgeon, D.; Prusevich, A.; Green, P.; Glidden, S.; Bunn, S. E.; Sullivan, C. A.; Reidy Liermann, C.; Davies, P. M. Global threats to human water security and river biodiversity. *Nature* **2010**, *467*, 555−561.

(2) Nyenje, P. M.; Foppen, J. W.; Uhlenbrook, S.; Kulabako, R.; Muwanga, A. Eutrophication and nutrient release in urban areas of sub-Saharan Africa—A review. *Sci. Total Environ.* **2010**, *408*, 447−455.

(3) Liu, J. G.; Raven, P. H. China's environmental challenges and implications for the world. *Crit. Rev. Env. Sci. Tec.* **2010**, *40* (9−10), 823−851.

(4) Qu, J.; Fan, M. The current state of water quality and technology development for water pollution control in China. *Crit. Rev. Environ. Sci. Technol.* **2010**, *40* (6), 519−560.

(5) Hu, H.; Yang, Q.; Lu, X.; Wang, W. C.; Wang, S. S.; Fan, M. H. Air pollution and control in different areas of China. *Crit. Rev. Environ. Sci. Technol.* **2010**, *40* (6), 452−518.

(6) Wei, B. G.; Yang, L. S. A review of heavy metal contaminations in urban soils, urban road dusts and agricultural soils from China. *Microchem. J.* **2010**, *94* (2), 99−107.

(7) Probe International. *Beijing's Water Crisis: 1949−2008 Olympics, 2010 Update*; Probe International Beijing Group: June 2008. Available at http://probeinternational.org/library/wp-content/uploads/2011/07/Beijing-Water-Report-2010-Update.pdf. Accessed 18/02/2012.

(8) Xie, J. *Addressing China's Water Scarcity*; World Bank: Washington, DC, 2008.

(9) Jiang, Y. China's water scarcity. *J. Environ. Manage.* **2009**, *90* (11), 3185−3196.

(10) Zhang, Y.; Xia, J.; Chen, J.; Zhang, M. Water quantity and quality optimization modeling of dams operation based on SWAT in Wenyu River Catchment, China. *Environ. Monit. Assess.* **2010**, 1−22.

(11) Liu, J.; Qin, D.; Wang, H.; Wang, M.; Yang, Z. Dualistic water cycle pattern and its evolution in Haihe River basin. *Chin. Sci. Bull.* **2010**, *55* (16), 1688−1697.

(12) Hong, Y.; Luan, S. China's Water Security. *Prog. Safety Sci. Technol.* **1998**, 835−842.

(13) Li, L.-Q.; Yin, C.-Q.; He, Q.-C.; Kong, L.-L. First flush of storm runoff pollution from an urban catchment in China. *J. Environ. Sci-China* **2007**, *19* (3), 295−299.

(14) Kahrl, F.; Li, Y.; Su, Y.; Tennigkeit, T.; Wilkes, A.; Xu, J. Greenhouse gas emissions from nitrogen fertilizer use in China. *Environ. Sci. Policy* **2010**, *13* (8), 688−694.

(15) Shi, Y.; Xiao, J.; Shen, Y. Landscape pattern change and associated environmental implications in the Haihe River Basin, China. *ISPRS J. Photogramm. Remote Sens.* **2008**, *37* (Part B4), 569−574.

(16) Anderson, D. M.; Glibert, P. M.; Burkholder, J. M. Harmful algal blooms and eutrophication: Nutrient sources, composition, and consequences. *Estuaries* **2002**, *25* (4B), 704−726.

(17) Heisler, J.; Glibert, P. M.; Burkholder, J. M.; Anderson, D. M.; Cochlan, W.; Dennison, W. C.; Dortch, Q.; Gobler, C. J.; Heil, C. A.; Humphries, E.; Lewitus, A.; Magnien, R.; Marshall, H. G.; Sellner, K.; Stockwell, D. A.; Stoecker, D. K.; Suddleson, M. Eutrophication and harmful algal blooms: A scientific consensus. *Harmful Algae* **2008**, *8* (1), 3−13.

(18) Diaz, R. J.; Rosenberg, R. Spreading dead zones and consequences for marine ecosystems. *Science* **2008**, *321* (5891), 926−929.

(19) Wang, J. H.; Wu, J. Y. Occurrence and potential risks of harmful algal blooms in the East China Sea. *Sci. Total Environ.* **2009**, *407* (13), 4012−4021.

(20) Wang, Z. Y.; Wu, Y.; Wang, G. Eutrophication and red tides as consequences of economic development. *Int. J. Sediment Res.* **2001**, *16* (4), 508−518.

(21) Labasque, T.; Chaumery, C.; Aminot, A.; Kergoat, G. Spectrophotometric Winkler determination of dissolved oxygen: Re-examination of critical factors and reliability. *Mar. Chem.* **2004**, *88* (1−2), 53−60.

(22) Zhang, H. H.; Brown, D. F. Understanding urban residential water use in Beijing and Tianjin, China. *Habitat Int.* **2005**, *29* (3), 469−491.

(23) Liu, X.; Ju, X.; Zhang, Y.; He, C.; Kopsch, J.; Fusuo, Z. Nitrogen deposition in agroecosystems in the Beijing area. *Agr. Ecosyst. Environ.* **2006**, *113* (1−4), 370−377.

(24) Huang, R.; Zhu, M.; Yang, P. *Analysis on Characteristics of Agricultural Non-Point Source Pollution in Haihe River Basin*; School of The Chinese Academy of Agricultural Sciences: Beijing, China, 2009. Available at http://www.bmtfi.com/upload/product/201005/2009shzyhy04a4.pdf. Accessed 18/02/2012.

(25) Jia, Y.; Zhao, H.; Niu, C.; Jiang, Y.; Gan, H.; Xing, Z.; Zhao, X.; Zhao, Z. A WebGIS-based system for rainfall-runoff prediction and real-time water resources assessment for Beijing. *Comput. Geosci.* **2009**, *35* (7), 1517−1528.

(26) Li, X. Pressure of water shortage on agriculture in arid region of China. *Chin. Geogr. Sci.* **2003**, *13* (2), 124−129.

(27) Foster, S.; Garduno, H.; Evans, R.; Olson, D.; Tian, Y.; Zhang, W.; Han, Z. Quaternary Aquifer of the North China Plain—Assessing and achieving groundwater resource sustainability. *Hydrogeol. J.* **2004**, *12* (1), 81−93.

(28) Camargo, J. A.; Alonso, A. Ecological and toxicological effects of inorganic nitrogen pollution in aquatic ecosystems: A global assessment. *Environ. Int.* **2006**, *32* (6), 831−849.

(29) Rong, Q. Comparison of Nutrient Removal Performance between A2/O and Inverted A2/O Processes and Optimization Studies. PhD Thesis; Graduate School of Chinese Academy of Sciences: Beijing, China, 2011.

(30) Liu, Y. Phosphorus flows in China, Physical Profiles and Environmental Regulation. PhD Thesis; Wageningen University: Wageningen, Netherlands, 2005.

(31) Aneja, V. P.; Bunton, B.; Walker, J. T.; Malik, B. P. Measurement and analysis of atmospheric ammonia emissions from anaerobic lagoons. *Atmos. Environ.* **2001**, *35*, 1949−1958.

(32) Qu, H. J.; Kroeze, C. Past and future trends in nutrients export by rivers to the coastal waters of China. *Sci. Total Environ.* **2010**, *408* (9), 2075−2086.

(33) Ma, X. Nitrogen flux analysis and its implications for environmental management in Huizhou, China. PhD Thesis; University of Hong Kong: Hong Kong, 2005.

(34) Boyer, E. W.; Howarth, R. W. *The Nitrogen Cycle at Regional to Global Scales*; Kluwer Academic Publishers: Dordrecht, Netherlands, 2002.

(35) Zessner, M.; Lindtner, S. Estimations of municipal point source pollution in the context of river basin management. *Water Sci. Technol.* **2005**, *52* (9), 175−182.

(36) Chambers, P. A.; Guy, M.; Roberts, E. S.; Charlton, M. N.; Kent, R.; Gagnon, C.; Grove, G.; Foster, N. *Nutrients and Their Impact on the Canadian Environment*; Environment Canada: Hull, Quebec, Canada, 2001. Available at http://publications.gc.ca/collections/Collection/En21-205-2001E-2.pdf. Accessed 18/02/2012.

(37) Bai, N.; Chen, S.; Guo, P.; Zhang, K.; Du, M. An eco-environmental database system for C, N, S, and P biogeochemical cycling in Haihe river basin. *Acta Sci. Circum.* **1991**, *11* (2), 157−165.

(38) Ye, C. Pollution and protection of Bohai Bay. *Mar. Pollut. Bull.* **1991**, *23*, 15−18.

(39) Liu, C.; Wang, Z.; He, Y. Water pollution in the river mouths around Bohai Bay. *Int. J. Sediment Res.* **2003**, *18* (4), 326−332.

(40) Turner, R. E.; Rabalais, N. N. Linking landscape and water quality in the Mississippi River Basin for 200 years. *Bioscience* **2003**, *53* (6), 563−572.

(41) Billen, G.; Garnier, J. River basin nutrient delivery to the coastal sea: Assessing its potential to sustain new production of non-siliceous algae. *Mar. Chem.* **2007**, *106* (1−2), 148−160.

(42) Behrendt, H. Point and Diffuse Load of Pollutants in the Rhine River Basin. In *International Association of Theoretical and Applied Limnology, Proceedings*; Sladeckova, A., Ed.; E. Schweizerbart Science Publishers: Stuttgart, Germany, 1994; Vol. *25* (part 3), pp 1922−1925.

(43) Meybeck, M. Carbon, nitrogen, and phosphorus transport by world rivers. *Am. J. Sci.* **1992**, *282*, 401−450.

(44) van Dijk, G. M.; Marteijn, E. C. L.; Schulte-Wülwer-Leidig, A. Ecological rehabilitation of the River Rhine: Plans, progress and perspectives. *Regul. Rivers* **1995**, *11* (3−4), 377−388.

(45) Billen, G.; Garnier, J.; Nemery, J.; Sebilo, M.; Sferratore, A.; Barles, S.; Benoit, P.; Benoit, M. A long-term view of nutrient transfers through the Seine river continuum. *Sci. Total Environ.* **2007**, *375* (1−3), 80−97.

(46) Wang, M.-J. Land application of sewage sludge in China. *Sci. Total Environ.* **1997**, *197* (1−3), 149−160.

(47) Fatta-Kassinos, D.; Meric, S.; Nikolaou, A. Pharmaceutical residues in environmental waters and wastewater: Current state of knowledge and future research. *Anal. Bioanal. Chem.* **2011**, *399* (1), 251−275.

(48) Ren, H.; Liu, H.; Qu, J.; Berg, M.; Qi, W.; Xu, W. The influence of colloids on the geochemical behavior of metals in polluted water using as an example Yongdingxin River, Tianjin, China. *Chemosphere* **2010**, *78* (4), 360−367.

(49) Qi, W.; Liu, H.; Qu, J.; Hu, C.; Lan, H.; Berg, M.; Ren, H.; Xu, W. Polycyclic aromatic hydrocarbons in effluents from wastewater treatment plants and receiving streams in Tianjin, China. *Environ. Monit. Assess.* **2011**, *177* (1), 467−480.

(50) Chen, S.; Wu, W.; Hu, K.; Li, W. The effects of land use change and irrigation water resource on nitrate contamination in shallow groundwater at county scale. *Ecol. Complex* **2010**, *7* (2), 131−138.

(51) Zhao, B.-Z.; Zhang, J.-B.; Flury, M.; Zhu, A.-N.; Jiang, Q.-A.; Bi, J.-W. Groundwater contamination with NO_3-N in a wheat-corn cropping system in the North China Plain. *Pedosphere* **2007**, *17* (6), 721−731.