Environmental Science & Technology

Article

pubs.acs.org/est

Organic Micropollutants in Rivers Downstream of the Megacity Beijing: Sources and Mass Fluxes in a Large-Scale Wastewater Irrigation System

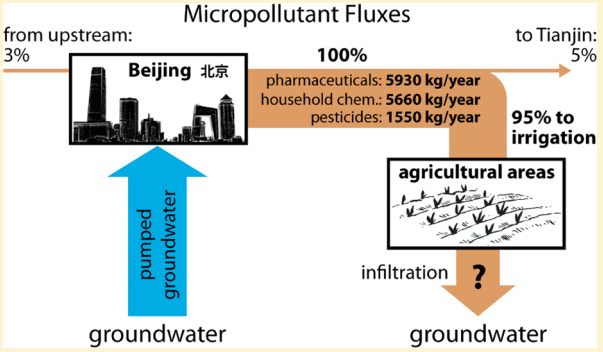
Florian Heeb,[†] Heinz Singer,*[,†] Benoît Pernet-Coudrier,[†] Weixiao Qi,[‡] Huijuan Liu,[‡] Philipp Longrée,[†] Beat Müller,[†] and Michael Berg*[,†]

[†]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, China

Supporting Information

ABSTRACT: The Haihe River System (HRS) drains the Chinese megacities Beijing and Tianjin, forming a large-scale irrigation system severely impacted by wastewater-borne pollution. The origin, temporal magnitudes, and annual mass fluxes of a wide range of pharmaceuticals, household chemicals, and pesticides were investigated in the HRS, which drains 70% of the wastewater discharged by 20 million people living in Beijing. Based on Chinese consumption statistics and our initial screening for 268 micropollutants using high-resolution mass spectrometry, 62 compounds were examined in space and time (2009−2010). The median concentrations ranged from 3 ng/L for metolachlor to 1100 ng/L for benzotriazole and sucralose. Concentrations of carbendazim, clarithromycin, diclofenac, and diuron exceed levels of ecotoxicological concern. Mass-flux analyses revealed that pharmaceuticals (5930 kg/year) and most household chemicals (5660 kg/year) originated from urban wastewaters, while the corrosion inhibitor benzotriazole entered the rivers through other pathways. Total pesticide residues amounted to 1550 kg/year. Per capita loads of pharmaceuticals in wastewater were lower than those in Europe, but are expected to increase in the near future. As 95% of the river water is diverted to irrigate agricultural soil, the loads of polar organic micropollutants transported with the water might pose a serious threat to food safety and groundwater quality.



INTRODUCTION

The rapid population growth occurring in megacities, especially in Africa and Asia, places increasing pressure on available surface and groundwater resources.[1] Furthermore, wastewater from urban sources is often used for irrigation in regions where water resources are scarce, particularly in developing and emerging countries.[2,3] In water-scarce areas surrounding megacities, this can lead to the installation of large-scale irrigation systems in which urban wastewater constitutes a substantial portion of the water used for the irrigation of adjacent agricultural areas.[4−6]

Increasing contamination of aquatic systems by polar organic micropollutants is a major problem for aquatic life, as well as for human health, as they are highly mobile and often of toxicological concern.[7] Pharmaceuticals and household chemicals, as well as biocides and other classes of organic micropollutants, are being increasingly discharged with wastewater to surface water environments.[7,8] Several authors document how conventional wastewater treatment often fails to remove polar organic micropollutants.[9−12] Hence, polar organic micropollutants have the potential to cause considerable problems in wastewater irrigation systems.[13] For example, Muñoz et al.[14] identified pharmaceuticals as a primary environmental risk associated with wastewater irrigation based on a risk assessment completed in Spain. However, risks and behaviors of organic micropollutants in wastewater irrigation are still poorly understood.[3]

An illustrative example is the Haihe River System (HRS), which connects the megacities of Beijing and Tianjin and is located within the water-scarce area of the North China Plain (NCP). Increasing overexploitation of limited water resources for agriculture and for the vastly growing urban agglomerations of the NCP have led to a steady decline of the groundwater table by about 0.5 m per year, as well as to the drying up of many rivers.[15−18] In the region of the megacity Beijing, water scarcity is particularly problematic due to extensive overuse and pollution of the available water resources.[19,20] Within Beijing, the groundwater table has dropped locally by up to 100−300 m, leading to ground subsidence of several meters.[21] Recent

Received: May 12, 2012
Revised: July 16, 2012
Accepted: July 18, 2012
Published: July 30, 2012

   dx.doi.org/10.1021/es301912q | Environ. Sci. Technol. 2012, 46, 8680−8688

research showed that the discharge of rivers downstream of Beijing is heavily influenced by wastewater from the megacity.[22,23] Due to these large loads of wastewater, the river system is oxygen-depleted and highly eutrophic, with toxic levels of nitrite and ammonia being frequently observed.[22] The treated wastewater accounts for 93% of the total water discharge (Supporting Information (SI) Figure S1), corresponding to the water consumption of some 14 million people, representing 70% of the population of Beijing's urban area. About 4% of the river discharge can be attributed to raw sewage from upstream Beijing.[22] The water consumed in Beijing is mainly sourced from groundwater. At the same time, over 90% of the discharge is used for irrigation in agricultural areas within approximately 100 km downstream of Beijing.[22] Hence, this river stretch forms a mega-scale wastewater irrigation system that is almost fully decoupled hydrologically from the up- and downstream areas.

The available information concerning polar organic micropollutants in the HRS is very limited to date. Three recent studies focused on the removal efficiency of selected WWTPs of certain micropollutants in Beijing.[24−26] The mass fluxes of micropollutants in the river system, particularly their influence on the large adjacent agricultural areas, remain unknown.

This study aims to improve the understanding of the load dynamics of polar organic micropollutants within a large-scale wastewater irrigation system in the water-scarce area of the megacity Beijing. First, occurrence and concentration ranges of micropollutants within the HRS are presented. Based on detailed discussions of three lead compounds (climbazole, benzotriazole, and atrazine), the flow dynamics of micropollutants in the HRS are then assessed. Finally, potential risks associated with the loads of organic micropollutants are identified, and implications for Beijing, as well as globally, are discussed.

METHODS

River System. We investigated the 175-km-long stretch of the HRS (Wenyu River and North Canal) that reaches from upstream Beijing to Tianjin (Figure 1). The water budget of this part of the HRS has been recently assessed.[22] Because most of its upstream tributaries ran dry, the discharge from the Shahe Reservoir currently accounts for an average of 1.1 m^3/s. Downstream, the discharge of the Wenyu River increases continuously as wastewater from the urban area of Beijing enters the river through four main tributaries, adding up to a total discharge of 32 m^3/s downstream of Beijing (Figure 1; Figure S1).

Two major channels divert the water from the main river to the Chaobaixin River and the Qinglongwan River for irrigation. Daily, weekly, or seasonal periodicity was not apparent in the discharge behavior of the rivers.[22] Conversely, fluctuations in discharge are controlled by the operation schemes of the dams.

The NCP is characterized by a continental climate. In 2009 the annual precipitation in the area of Beijing amounted to 480 mm, of which 80% fell in the wet summer season between June and September [27] (Figure S2). Despite being one of the areas with the lowest water availability in China, the region between Beijing and Tianjin is one of China's primary agricultural areas, dominated mainly by the production of wheat and corn (Figure 1).[18,28] The fields are irrigated by flooding through an extensive network of irrigation channels fed either by water from the rivers, or by water pumped from groundwater wells. Although groundwater covers 65% of the irrigation demand,[29] 95% of the

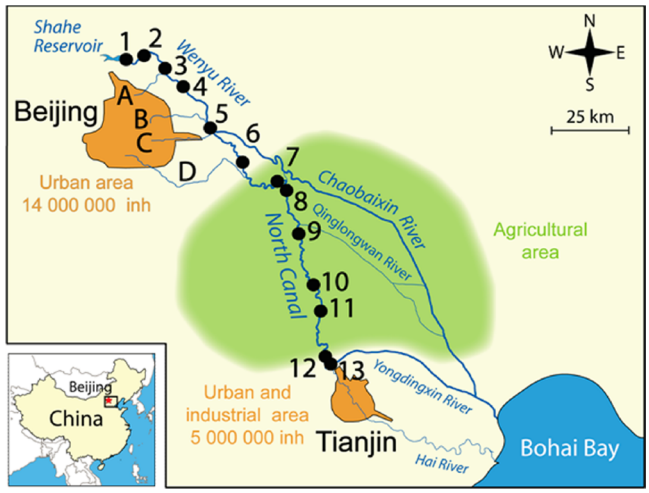


Figure 1. Map of the HRS between Beijing and Tianjin. Downstream of the Shahe Reservoir in the north, the river is referred to as the Wenyu River in the upstream portion, and as the North Canal further downstream. The Chaobaixin and Qinglongwan Rivers are two main diversions of water to the Yongdingxin River in the south. The numbers 1 to 13 mark the sites that were sampled in this study. The letters A−D denote the main tributaries draining the wastewater effluents from the urban area of Beijing into the main river. A: Qing River; B: Beixiao River; C: Tonghui River; D: Liangshui River (based on Pernet-Coudrier et al.[22]).

total discharge of the Wenyu River and North Canal is withdrawn for irrigation. Only 5% remains in the river channel at Tianjin (Figure 1, site 13).

Sampling. For the analysis of the spatial variation in micropollutant concentrations, two sampling campaigns comprising all 13 sampling sites were performed: one during the dry season in April 2009, and one during the wet season in July 2009. Additionally, sites 1, 5, 9, 12, and 13 were sampled monthly for a 14-month period from April 2009 to June 2010. For sites 1, 5, 9, and 13, gauge readings of daily river water discharge were acquired. River water samples were obtained from a bridge or dam using a bucket. The five WWTPs with the highest treatment capacities in Beijing (Qinghe, Jiuxianqiao, Beixiaohe, Gaobeidian, and Xiaohongmen) were sampled three times (Table S1, Figure S3). In May 2010 and December 2010, grab samples of the inlets and outlets were taken and time-proportional 24-h composite samples of the influents and effluents were collected in March 2011. The five sampled WWTPs are responsible for 90% of Beijing's wastewater discharge into the Wenyu River. The daily water discharge of these five WWTPs was obtained from the facility managers.

Screening and Compound Selection. Two of the initial samples (June 2009, sites 7 and 12) were screened by LC-high-resolution tandem mass spectrometry[30,31] for 268 pharmaceuticals, pesticides, biocides, industrial chemicals, household chemicals, and associated metabolites that were found to be relevant in China. For this purpose, Chinese production and export statistics of pharmaceuticals for 2009,[32] as well as a summary of the demand of major pesticides in China were assessed for the same year[33] (Tables S7−S8). Of the 100 most consumed pharmaceuticals, 34 were detected by the screening method in concentrations >LOD (limit of detection). Many of the remaining substances are known to show either strong sorption or fast degradation under environmental conditions (e.g., tetracycline, oxytetracycline, amoxicillin, penicillin G,

dx.doi.org/10.1021/es301912q | Environ. Sci. Technol. 2012, 46, 8680−8688

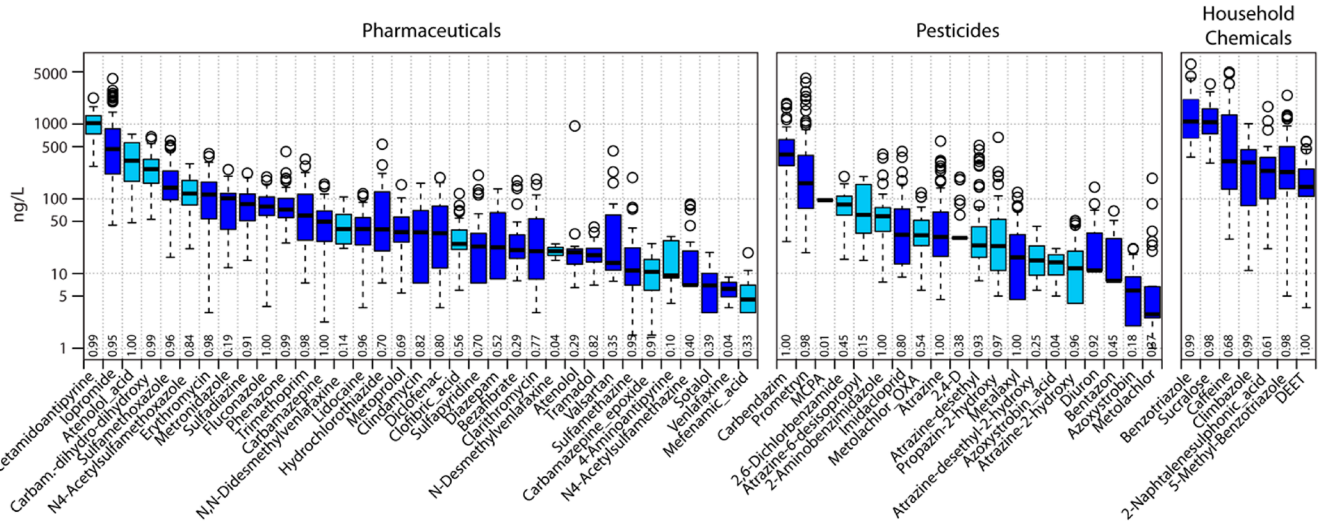


Figure 2. Concentration ranges of pharmaceuticals, pesticides, and household chemicals in all samples of the examined sections of the Haihe River from April 2009 to June 2010. Parent compounds are shown in dark blue, metabolites are in light blue. The solid bar marks the median. The box denotes the 0.25 and 0.75 percentiles. The whiskers mark the last value within a range of 1.5 times the 0.25 and 0.75 percentiles. Outliers are marked by dots. For the statistical analysis, only values >LOD were considered. Values between the LOD and the LOQ were considered as 0.5 × LOQ. The values at the *x*-axis show the decimal proportion of values >LOD.

cephalexin, and paracetamol). Of the 20 most widely used pesticides, 7 were detected by the screening method. Based on the results of this initial screening, a comprehensive set of 62 micropollutants was examined in depth.

Quantification of Micropollutants. Surface water and wastewater samples (250 mL) were filled in baked glass bottles (Schott), and shipped by airmail at 4 °C within 3 days to Eawag, where the samples were stored at −20 °C until analysis. Immediately prior to analysis, the thawed samples were filtered through glass-fiber filters (GF/F, pore size 0.7 μm, Whatman), and isotope-labeled internal standard (IS) solution was added.

Eighty-four samples from the Haihe River and 22 samples from wastewater inflow and effluent were analyzed for 62 micropollutants using a fully automated solid-phase extraction (SPE) system, coupled directly to a liquid chromatography (LC) tandem mass spectrometer. The online SPE-LC setup was similar to the one reported by Stoob et al.[34] The analytical method utilized was similar to the one described by Singer et al.[35] (Text S1−S3, Tables S2−S4). Including calibration and quality control, over 20 000 measurements of individual substances were performed.

Quantification was carried out with 44 isotope-labeled internal standards (IS). For analytes for which no structurally identical IS was available, the IS with the most similar retention times was used for quantification. The average relative recoveries were within 85−112% for all compounds excluding imidacloprid (77%) and clindamycin (132%). Details concerning quality assurance, including limit of detection (LOD), limit of quantification (LOQ), relative recoveries, and uncertainties are provided in the SI Text S4−S5 and Table S5.

Mass Flows. For the sampling sites (j) with available daily discharge data (sites 1, 5, and 9), the annual loads of all substances (i) were calculated for the period of July 2009 to June 2010 based on the concentrations measured in the river via

$$L_{\mathrm{river},i,j} = \sum_{m=1}^{12} \bar{Q}_{\mathrm{daily},m,j} \times c_{\mathrm{river},i,j,m} \quad (1)$$

where $\bar{Q}_{\mathrm{daily},m,j}$ is the monthly average of the daily discharge for the month m at site j and $c_{\mathrm{river},i,j,m}$ is the measured concentration of substance i at site j for the month m.

For all sites (j) the annual wastewater-borne load of all substances (i) was calculated based on the inputs of Beijing's WWTPs via

$$L_{\mathrm{WW}i,j} = L_{\mathrm{WW}i,j-1} \times \left(\frac{Q_{r,j}}{Q_{r,j} + Q_{\mathrm{sc},(j,j-1)}} \right) + Q_{\mathrm{WW}(j,j-1)} \times c_{\mathrm{WW}i,(j,j-1)} \quad (2)$$

where $Q_{\mathrm{WW}(j,\,j-1)}$ is the annual discharge of wastewater entering the river between sites $j-1$ and j; $c_{\mathrm{WW}i,(j,\,j-1)}$ is the average concentration of substance i in the wastewater discharged between the two sites, calculated based on samples obtained from Beijing's five major WWTPs (see Text S6); $Q_{r,j}$ is the average annual discharge of the main river at site j; and $Q_{\mathrm{sc}(j,\,j-1)}$ is the discharge withdrawn from the main river by side channels between $j-1$ and j. For calculation purposes, the spatial resolution of sites j was chosen so that either $Q_{\mathrm{WW}\,(j,\,j-1)}$ or $Q_{\mathrm{sc}\,(j,\,j-1)}$ is equal to zero.

The mass balance equation 2 implies conservative behavior of the micropollutants within the river. Hence, if $L_{\mathrm{river},i,\,j}$ deviates significantly from $L_{\mathrm{WW}i,j}$, this indicates either the presence of another source of the substance in addition to the wastewater or a transformation process within the river. It has to be considered that L_{river} possibly underestimates contributions from short-time peak concentrations that were not covered by the available samples. However, over the sampling period, concentrations were relatively constant in the river for many pharmaceuticals.

RESULTS AND DISCUSSION

Concentration Ranges. Generally, the spectrum of pharmaceuticals found in the HRS during the 14-month study period is similar to results reported for surface waters in Europe and the United States.[10,36] 35 different pharmaceuticals and metabolites as well as 7 household chemicals and 20

dx.doi.org/10.1021/es301912q | Environ. Sci. Technol. 2012, 46, 8680−8688

pesticides were detected totaling 62 compounds (Figure 2, Table S9). Most micropollutants were frequently present; 28 of the 62 were detected in more than 90% of the samples. Ten substances had peak concentrations >1000 ng/L (4-acetamidoantipyrine, benzotriazole, methyl benzotriazole, carbendazim, climbazole, caffeine, iopromide, naphtalenesulphonic acid, prometryn, and sucralose). Sucralose (1060 ng/L), benzotriazole (1090 ng/L), and 4-acetamidoantipyrine (1030 ng/L) showed the highest median concentrations. The production of sucralose in China increased considerably since 2009, when corresponding patents expired,[37] and these high levels of sucralose are indicative of substantial consumption in Beijing.

4-Acetamidoantipyrine (a primary metabolite of metamizole) ranged between 270 and 2200 ng/L, which obviously reflects the fact that metamizole is the second most consumed analgesic in China, after the nonpersistent paracetamol. The antifungal agent climbazole, which is mainly used in antidandruff shampoos, was detected in 99% of all samples (mean: 310 ng/L). Prior to this study, climbazole had rarely been detected in aquatic systems.[38] The annually averaged sum of the concentrations of all quantified micropollutants amounted to 11.4 μg/L (7.8−17.9 μg/L) downstream of Beijing at site 9.

To evaluate the ecotoxicological risk of the micropollutant concentrations, chronic and acute effect concentrations were compared with annual averaged and maximum concentrations. Environmental Quality Standards (EQS) as defined by the European Union according to the Technical Guidance Document for EQS (TGD for EQS) were taken from the literature[39−43] to retrieve chronic and acute effect concentrations, whereas data was only available for 16 of the 62 detected compounds. EQS expressed as an annual average value (AA-EQS) are defined for long-term exposure (chronic effects), whereas maximum allowable concentrations (MAC-EQS) are used to assess short-term exposure (acute effects). MAC-EQS and AA-EQS were exceeded for carbendazim, clarithromycin, diclofenac, and diuron (see Table S10). For carbendazim, the MAC-EQS were exceeded in 29% of the samples. On average, 45 micropollutants were detected per sample, and thus the combined effects of micropollutants should also be considered.[44] In addition to the ecotoxicological impact of micropollutants, the aquatic ecosystem of the HRS is already heavily stressed by other factors such as oxygen depletion and excessive nutrient concentrations.[22]

Mass Fluxes. In Figure 3, the wastewater-borne loads of micropollutants at site 9 downstream of Beijing ($L_{WW,9}$) are compared to loads observed in the river at site 9 ($L_{river,9}$). Whereas the measured load in the river at site 9 ($L_{river,9}$) comprises all upstream inputs from urban and agricultural sources apart from the diverted amount (irrigation and distributaries), the calculated wastewater-borne loads at site 9 ($L_{WW,9}$) incorporate only the amount stemming from the upstream WWTPs, corrected for the withdrawn proportion. $L_{WW,9}$ and $L_{river,9}$ were largely comparable for most pharmaceuticals (Figure 3; purple, $L_{WW,9}/L_{river,9}$ = 1.1 on average), which shows that observed loads are well explained by the wastewater inputs. This also applies to the household chemicals climbazole and sucralose (Figure 3; green, $L_{WW,9}/L_{river,9}$ = 0.9 and 1.3, respectively). These results indicate that the main sources of these compounds are households and the main input pathways are the discharges of Beijing's WWTPs.

$L_{WW,9}$ is considerably smaller than $L_{river,9}$ for most pesticides (Figure 3; orange, $L_{WW,9}/L_{river,9}$ = 0.4 on average), as are the corrosion inhibitors benzotriazole (L_{WW}/L_{river} = 0.1) and

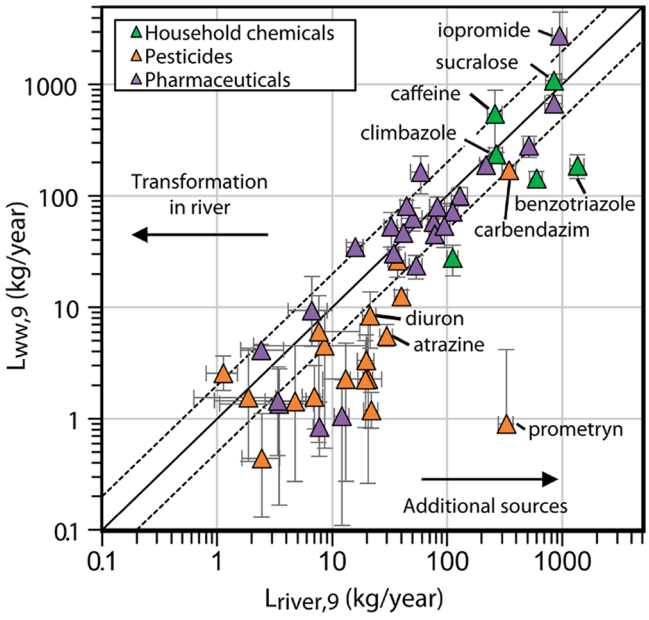


Figure 3. Wastewater-borne loads of micropollutants at site 9 downstream of Beijing ($L_{WW,9}$) versus observed loads at site 9 ($L_{river,9}$). Only compounds that were detectable in the wastewater and in the river are shown. The large uncertainties for the compounds with low loads are due to concentrations below the LOQs. Where $L_{WW,9}$ is similar to $L_{river,9}$ (factor ±2), the wastewater inputs from Beijing explain the observed loads well. If $L_{WW,9}$ exceeds $L_{river,9}$, transformation of the compound in the river is likely. If $L_{WW,9}$ is smaller than $L_{river,9}$, the compound enters the river through additional (nonpoint) sources. The error bars denote the overall uncertainties (Text S5). Compounds discussed in detail are labeled in the figure.

methyl benzotriazole ($L_{WW,9}/L_{river,9}$ = 0.2). This points to unidentified major source(s) of these compounds in addition to the inputs from Beijing's WWTPs.

If $L_{WW,9}$ is significantly higher than $L_{river,9}$, this indicates that the compounds are removed/transformed within the river system, i.e. by degradation or sorption processes. According to the measurements and mass flux calculations, 550 kg of caffeine and 2760 kg of iopromide were discharged into the HRS per year via the treated wastewater ($L_{WW,9}$), while only 260 kg of caffeine and 960 kg of iopromide were recovered in the river ($L_{river,9}$). Whereas caffeine is known to degrade in natural environments,[45] X-ray contrast media, such as iopromide, are known to show strongly fluctuating concentrations in wastewater.[46] The high L_{WW}/L_{river} for iopromide could derive from the large uncertainties in L_{WW} due to the strongly fluctuating concentrations observed in the effluents of Beijing's WWTPs. Apart from these cases, most compounds did not seem to be substantially removed/transformed in the rivers.

The comparison between L_{WW} and L_{river} is a valuable tool to cluster the compound data according to major sources and sinks in the observed system, as a detailed evaluation of the situation for every individual compound is not always feasible. To corroborate the source-removal pattern illustrated in Figure 3, selected compounds representative of agricultural and urban sources are discussed in more detail taking all relevant information into account.

Sources in Urban Households. The antifungal agent climbazole is a typical example of a micropollutant that enters the river system via the discharge of Beijing's WWTPs. As it is mainly used in antidandruff shampoos, it is a typical example of

dx.doi.org/10.1021/es301912q | Environ. Sci. Technol. 2012, 46, 8680−8688

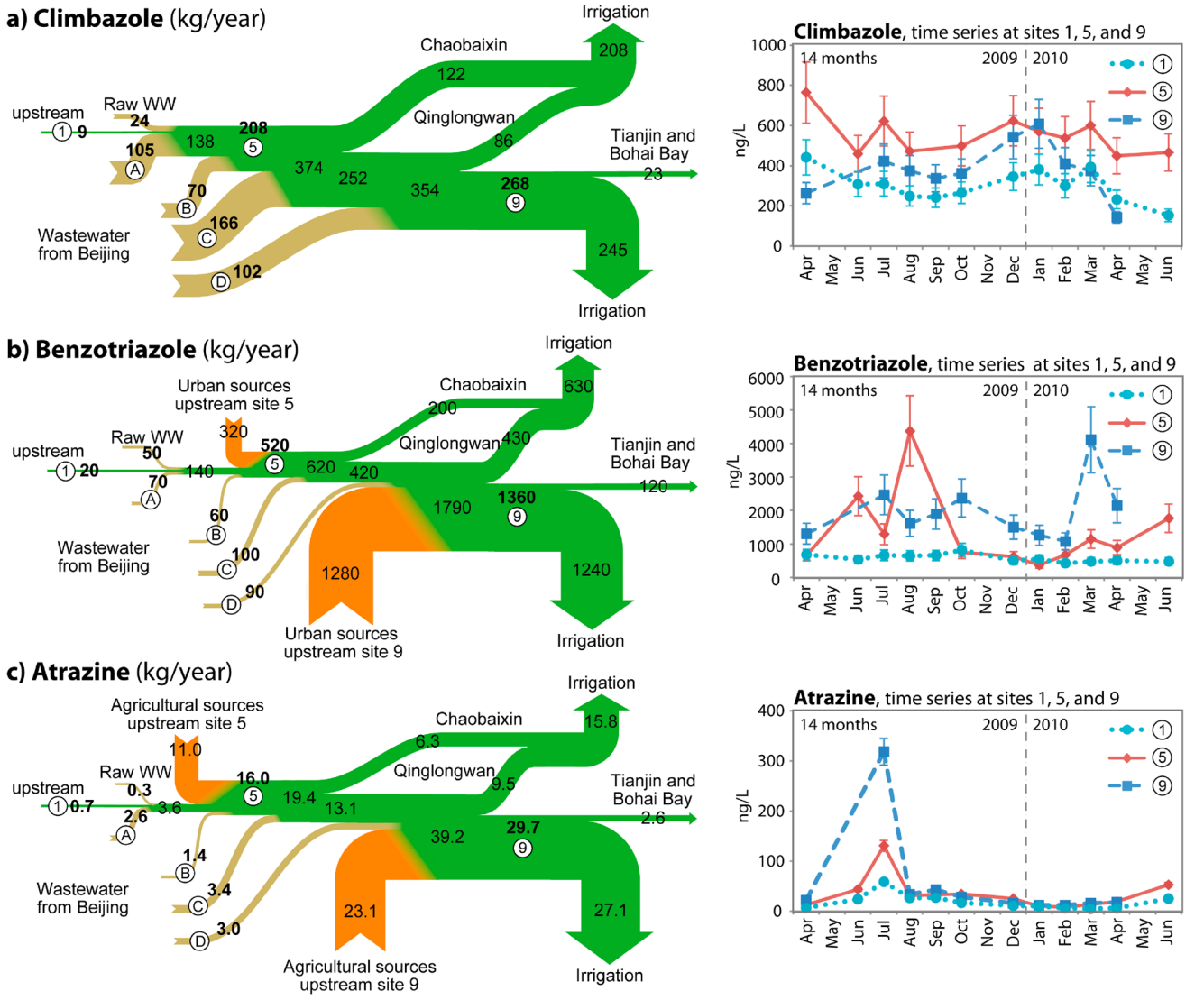


Figure 4. Mass flow diagrams (kg/year) and concentration time series (ng/L) for climbazole, benzotriazole, and atrazine. Mass flows that are directly based on measured concentrations are printed in bold. The encircled numbers 1, 5, and 9 denote sampling sites for the 14-month time series (right panels), where error bars indicate the uncertainties in the measurements (Text S5). Letters A–D mark the inflows of wastewater from the four main channels: Qing (A), Beixiao (B), Tonghui (C), and Liangshui (D). Loads from wastewater are shown in brown. Additional inputs required to balance the observed loads at sites 5 and 9 are fitted and illustrated in orange. Micropollutant concentrations at the branches of the Chaobaixin and Qinglongwan Rivers were assumed to be identical to concentrations in the main channel, right at the diversions (see Figure 1).

a household chemical. The total loads observed downstream of Beijing are considerable (476 kg/year), yet there is no information available about its behavior in the environment. The average removal rate of climbazole in the WWTPs of Beijing was 7% (Table S12). This suggests that the compound is stable in aquatic environments. However, photolysis cannot be excluded. The inputs of climbazole from Beijing's wastewater fit the loads observed at both sites 5 and 9 (Figure 4a). Contributions from the upstream areas are almost negligible. Concentrations of climbazole do not show an apparent seasonality, as they remained relatively constant over the year (Figure 4a). However, the two sampling campaigns (April and July 2009) at all 13 sites revealed a distinct increase in concentrations of climbazole between sites 3 and 4, where the first sewers of Beijing enter the river system (see Figure S4). Thus, these data confirm the dominating influence of Beijing's wastewater. The mass flow behavior of climbazole is representative of most pharmaceuticals and household chemicals for which degradation in the river system can be neglected.

For the widely used pharmaceuticals bezafibrate, carbamazepine, clarithromycin, diclofenac, and mefenamic acid, the per capita loads in raw wastewater were 6–300 times lower in Beijing than those reported for Europe.[10,47] For iopromide, sulfamethazine, sulfamethoxazole, sulfapyridine, and trimethoprim, the per capita loads lie in a range similar to the ones reported for Europe. Only for erythromycin and sulfadiazine were the per capita loads in Beijing significantly higher than reported values for Europe (Table S11). The market for pharmaceuticals in China grew by 26% in 2009 and is expected to double from 2009 to 2013.[48] The observed per capita loads today suggest that consumption of pharmaceuticals in Beijing has not yet reached European levels. However, it is likely that the loads of pharmaceuticals from Beijing's wastewater will increase considerably in the near future.

dx.doi.org/10.1021/es301912q | Environ. Sci. Technol. 2012, 46, 8680–8688

Removal in Wastewater Treatment. As mentioned above, a majority of Beijing's wastewater is treated. However, the investigated micropollutants are not always sufficiently removed via the conventional treatment processes applied in Beijing's major WWTPs, where removal rates averaged between +67% and −27%. An exception is caffeine, with 88% removal on average (see Table S12). Using more advanced treatment technologies such as ozonation, nanofiltration, reverse osmosis, or powdered activated carbon would facilitate enhanced removal of most organic micropollutants to a significant extent[10,49,50] and hence reduce the loads of wastewater-borne micropollutants in the river system. Advanced treatment is currently being tested in three Beijing WWTPs on a pilot scale, treating some 10% of their wastewater.[25,51] As an example, the total loads of climbazole discharged by Beijing could be reduced by around 70% if advanced treatment is installed for the full capacity of the 5 major WWTPs, assuming a removal rate of 90% in advanced treatment.

Additional Urban Sources. The spatial and temporal concentration pattern of the corrosion-inhibitor benzotriazole is an example for micropollutants originating mainly from other urban sources. Benzotriazole is known to be quite persistent in the aquatic environment.[52−54] It is therefore reasonable to assume conservative behavior in the river. There is a base load of benzotriazole in Beijing's wastewater (Figure 4b; brown) which likely originates from household applications in dishwashing detergents.[55] However, the base load is far too small to explain the observed loads in the river. This suggests additional input of benzotriazole (Figure 4b; orange) between sites 5 and 9. We cannot rule out short-term peak concentrations in the effluents of Beijing's WWTPs that were not captured by our sampling campaigns. However, this pathway may not be substantial, since the concentrations in the river at site 9 (mean 2050 ng/L) were always significantly higher than those observed in the WWTP effluents (mean 446 ng/L). The two extended sampling campaigns (April and July 2009) comprising all 13 sites revealed a distinct increase of benzotriazole concentrations between sites 5 and 6 (see Figure S4). There was no seasonality in the benzotriazole concentrations and yet there were considerable fluctuations over the studied time period (Figure 4b). Due to its corrosion-inhibiting properties, benzotriazole is also used in aircraft deicers and in heating and cooling systems. Therefore, wastewaters from industrial areas or from the Beijing international airport entering the river between sites 5 and 6 are the most probable source(s) of the unidentified benzotriazole input.

Similar characteristics apply to other abundantly occurring pesticides such as carbendazim, diuron, and prometryn. Since small-scale vegetable farming is common in urban areas of China,[56] this could be a substantial urban source. Also, minor parts of the loads of carbendazim and diuron seemed to originate from household applications for biocidal purposes, as was similarly reported for Europe.[57]

Compared to Europe, the per capita loads of benzotriazole and methyl benzotriazole in raw wastewaters were 5−9 times lower in Beijing.[10,47] For carbendazim, the per capita loads were 7−19 times higher in Beijing (Table S11). This could indicate a Beijing- or China-specific source of carbendazim from household applications.

An increase in advanced treatment capacities would only have a minor effect on the total loads of urban pesticides and corrosion inhibitors, as Beijing's WWTPs are not their main entry path. In contrast to climbazole, the total loads of benzotriazole would be reduced by a mere 10% if advanced treatment facilities were installed for the full capacity of the 5 major WWTPs. Thus regulatory measures to reduce the inputs directly at the corresponding sources are necessary for these micropollutants.

Agricultural Sources. The herbicide atrazine is a typical pesticide from agricultural sources (Figure 4c). The small loads of atrazine originating from the wastewater of Beijing's urban area (Figure 4c; brown) show that a minor fraction stems from household applications. Hence, there must be substantial sources upstream of sites 5 and 9 (Figure 4c; orange) to explain the observed loads. Atrazine concentrations in the river show a clear seasonality, with a distinct peak in July and levels near the LOQ in winter, as expected for agricultural applications (Figure 4c). The sampling campaign of all 13 sites in July 2009 showed that concentrations were strongly elevated in the agriculturally influenced areas upstream and downstream of Beijing and decreased in the urban areas of Beijing (Figure S4). This indicates that atrazine originates mainly from diffuse agricultural sources. The mean ratio of atrazine and its metabolite atrazine-desethyl was 0.8 (range 0.5−1.4) at site 9 downstream Beijing, suggesting that the atrazine entering the river is already considerably degraded. Generally, atrazine-desethyl exhibits mass-flow dynamics similar to atrazine. The observed peak of atrazine in July corresponds directly to a maximum in precipitation that occurred during the wet season (Figure S2). Hence, it seems that atrazine applied to crops in spring was flushed into the river by strong rain events in early summer. In July, the cornfields were intensely flooded for irrigation; hence, overflows from flooded fields are another possible input pathway. Atrazine is the only pesticide for which the primary source could be allocated to the agricultural areas outside of Beijing. Thus, inputs of micropollutants from the agricultural areas play a minor role compared to the influence of the megacity Beijing.

Total Loads. Of the total annual loads of all detected micropollutants, 95% end up on agricultural fields by way of irrigation (see abstract graphic). The total annual loads of organic micropollutants in the HRS amount to 13 140 ± 620 kg/year (±standard deviation, see Text S5). Of this total, pharmaceuticals and metabolites contribute 5930 ± 440 kg/year, pesticides and metabolites contribute 1550 ± 140 kg/year, and household chemicals contribute 5660 ± 350 kg/year. The specific loads measured at sites 1, 5, and 9 are presented in Figure 5. Urban sources clearly dominate the total loads of micropollutants. It must be taken into account that the list of quantified compounds, which was designed to be as broad and representative as possible, may lack some locally relevant micropollutants. Hence, the total load may be underestimated.

Threats to Groundwater Resources. The presented mass fluxes suggest important implications for the cycles of water and micropollutants between the urban and agricultural areas downstream of Beijing (see abstract graphic). Groundwater accounts for 75% of Beijing's water consumption.[17,20] Within the urban water cycle this water becomes enriched with numerous contaminants. Many polar organic micropollutants are only partially removed in the WWTPs of Beijing. As a result of scarce precipitation, the water flowing in the HRS consists of >95% treated and untreated wastewater and is used almost entirely to irrigate crops (see Figure S1), thereby depositing considerable loads of pollutants on agricultural soil. Moreover, irrigation contributes substantially to groundwater recharge in the North China Plain.[58−60] Micropollutants may accumulate in

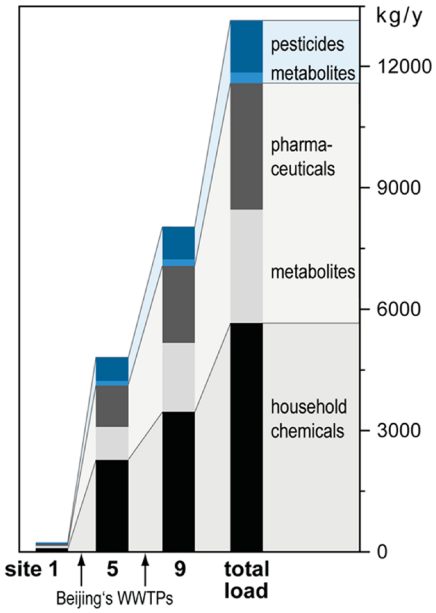


Figure 5. Annual loads of organic micropollutants (kg/year) drained through the Wenyu River (sites 1 and 5), the North Canal (site 9), and the total loads in 2009/2010. The total load of micropollutants is the sum of the load at site 9 and the diverted load to the Chaobaixin and the Qinglongwan Rivers.

soil and crops, may trigger resistance against antibiotics and fungicides, and may percolate to the subsurface and eventually reach the groundwater.[61] Although there is no information available about the behavior of micropollutants in the soil and subsurface of the Beijing−Tianjin region, studies in Mexico have shown several micropollutants originating from irrigation with urban wastewater accumulated in the aquifers.[62,63] Hence the huge loads of micropollutants discharged by 14 million people in Beijing can enter the food chain as well as contaminate the precious groundwater resources over the long-term. As groundwater resources are the main source of drinking water for the 100 million inhabitants of the region, there is an urgent need to investigate the fate of pollutants deposited on agricultural land.

Implications. *For Beijing.* As discussed above, consumption of pharmaceuticals in Beijing is likely to increase further. At the same time, the residential water demand of Chinese megacities is projected to grow steadily.[64] Preventing contamination of groundwater and drinking water resources is therefore of the utmost importance for sustainable development. An increase in advanced state-of-the-art wastewater treatment capacities in Beijing's WWTPs would considerably reduce the loads of pharmaceuticals and household chemicals. However, for micropollutants from urban point sources such as the corrosion-inhibitors benzotriazole and methyl benzotriazole or for pesticides from diffuse agricultural sources, which bypass the WWTPs, regulatory measures to reduce inputs directly at the sources are necessary.

International Context. Large-scale wastewater irrigation systems and the associated ecological and human risks of contamination of soil and groundwater with micropollutants, as discussed here for Beijing, are common issues in arid and semiarid regions around the globe. These regions typically share the following features: (i) large urban agglomeration, located in a water-scarce climate; (ii) low dilution of urban wastewater in the discharging rivers, and (iii) nearby agricultural areas with large demand for irrigation. Within the North China Plain, there are further urban agglomerations with several million inhabitants where these features apply (e.g., Shijiazhuang, Tanshang, Xuzhou, Baoding). On a worldwide scale, there are also many large-scale wastewater irrigation systems, such as, e.g., the megacities of Mexico City or Hyderabad (India).[4−6] Our present study highlights the threat created by the shortcuts among wastewater, soils, and groundwater, and may increase awareness of chemical risks for food safety and drinking water quality. The consumption of pharmaceuticals is increasing globally, especially in emerging economies.[48] At the same time, with vastly growing urban agglomerations[1] and increasing demands for irrigation,[65] the risks of accumulation of micropollutants due to large-scale wastewater irrigation systems are also likely to increase on a global scale.

■ ASSOCIATED CONTENT

Supporting Information

Additional information on the river system, treatment plants, detected compounds, analytical methods, quality assurance, and detailed figures and tables on concentrations, removal rates, and mass flows. This information is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: heinz.singer@eawag.ch (H.S.); michael.berg@eawag.ch (M.B.).

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, and Meng Qiao are acknowledged for excellent assistance in sampling campaigns. We thank Caroline Frank for the LC-MS support, Falk Dorusch and Alfred Lück for their technical assistance, Kathrin Fenner and Juliane Hollender for helpful comments on the manuscript, and Lee Bryant for language editing. Gauge readings for daily river water discharges were provided by the Hebei Bureau of the Hydrology and Water Resources Survey and by the Central Hydrology Station of Beijing. This study was funded by the External Cooperation Program of the Chinese Academy of Sciences, Grant GJHZ0908, and by the Sino-Swiss Science and Technology Cooperation Program of the Swiss State Secretariat for Education and Research, project IZL CZ2 123912.

■ REFERENCES

(1) Varis, O. Megacities, Development and Water. *Int. J. Water Resour. Dev.* **2006**, *22* (2), 199−225.

(2) Qadir, M.; Wichelns, D.; Raschid-Sally, L.; McCornick, P. G.; Drechsel, P.; Bahri, A.; Minhas, P. S. The challenges of wastewater irrigation in developing countries. *Agric. Water Manage.* **2010**, *97* (4), 561−568.

(3) Hamilton, A. J.; Stagnitti, F.; Xiong, X.; Kreidl, S. L.; Benke, K. K.; Maher, P. Wastewater Irrigation: The State of Play. *Vadose Zone J.* **2007**, *6* (4), 823.

(4) Siemens, J.; Huschek, G.; Siebe, C.; Kaupenjohann, M. Concentrations and mobility of human pharmaceuticals in the world's

largest wastewater irrigation system, Mexico City−Mezquital Valley. *Water Res.* **2008**, *42* (8−9), 2124−2134.
(5) Jimenez, B.; Chavez, A. Quality assessment of an aquifer recharged with wastewater for its potential use as drinking source: "El Mezquital Valley" case. *Water Sci. Technol.* **2004**, *50* (2), 269−276.
(6) Van Rooijen, D. J.; Turral, H.; Wade Biggs, T. Sponge city: water balance of mega-city water use and wastewater use in Hyderabad, India. *Irrig. Drain.* **2005**, *54* (S1), S81−S91.
(7) Schwarzenbach, R. P.; Escher, B. I.; Fenner, K.; Hofstetter, T. B.; Johnson, C. A.; von Gunten, U.; Wehrli, B. The Challenge of Micropollutants in Aquatic Systems. *Science* **2006**, *313* (5790), 1072−1077.
(8) Hollender, J.; Singer, H.; McArdell, C. S. Polar Organic Micropollutants In The Water Cycle. In *Dangerous Pollutants (Xenobiotics) in Urban Water Cycle*; Hlavinek, P., Bonacci, O., Marsalek, J., Mahrikova, I., Eds.; Springer: Netherlands, 2008; pp 103−116.
(9) Joss, A.; Keller, E.; Alder, A. C.; Göbel, A.; McArdell, C. S.; Ternes, T.; Siegrist, H. Removal of pharmaceuticals and fragrances in biological wastewater treatment. *Water Res.* **2005**, *39* (14), 3139−3152.
(10) Hollender, J.; Zimmermann, S. G.; Koepke, S.; Krauss, M.; McArdell, C. S.; Ort, C.; Singer, H.; von Gunten, U.; Siegrist, H. Elimination of Organic Micropollutants in a Municipal Wastewater Treatment Plant Upgraded with a Full-Scale Post-Ozonation Followed by Sand Filtration. *Environ. Sci. Technol.* **2009**, *43* (20), 7862−7869.
(11) Jones, O. H.; Voulvoulis, N.; Lester, J. Human Pharmaceuticals in Wastewater Treatment Processes. *Crit. Rev. Environ. Sci. Technol.* **2005**, *35* (4), 401−427.
(12) Göbel, A.; Thomsen, A.; McArdell, C. S.; Joss, A.; Giger, W. Occurrence and Sorption Behavior of Sulfonamides, Macrolides, and Trimethoprim in Activated Sludge Treatment. *Environ. Sci. Technol.* **2005**, *39* (11), 3981−3989.
(13) Fatta-Kassinos, D.; Kalavrouziotis, I. K.; Koukoulakis, P. H.; Vasquez, M. I. The risks associated with wastewater reuse and xenobiotics in the agroecological environment. *Sci. Total Environ.* **2011**, *409* (19), 3555−3563.
(14) Muñoz, I.; Gómez-Ramos, M. J.; Agüera, A.; Fernández-Alba, A. R.; García-Reyes, J. F.; Molina-Díaz, A. Chemical evaluation of contaminants in wastewater effluents and the environmental risk of reusing effluents in agriculture. *Trends Anal. Chem.* **2009**, *28* (6), 676−694.
(15) 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.
(16) Liu, C.; Xia, J. Water problems and hydrological research in the Yellow River and the Huai and Hai River basins of China. *Hydrol. Process.* **2004**, *18* (12), 2197−2210.
(17) Liu, J.; Cao, G.; Zheng, C. Sustainability of Groundwater Resources in the North China Plain. In *Sustaining Groundwater Resources*; Jones, J. A. A., Ed.; International Year of Planet Earth Series; Springer, 2011, pp 69−87.
(18) Yang, H.; Zehnder, A. China's regional water scarcity and implications for grain supply and trade. *Environ. Plan. A* **2001**, *33* (1), 79−95.
(19) Jiang, Y. China's water scarcity. *J. Environ. Manage.* **2009**, *90* (11), 3185−3196.
(20) 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 2/18/2012.
(21) Shalizi, Z. *Addressing China's Growing Water Shortages and Associated Social and Environmental Consequences*; The World Bank: Washington, DC, 2006.
(22) Pernet-Coudrier, B.; Qi, W.; Liu, H.; Müller, B.; Berg, M. Sources and Pathways of Nutrients in the Semi-Arid Region of Beijing−Tianjin, China. *Environ. Sci. Technol.* **2012**, *46* (10), 5294−5301.
(23) Qiao, M.; Zheng, Y. M.; Zhu, Y. G. Material flow analysis of phosphorus through food consumption in two megacities in northern China. *Chemosphere* **2011**, *84* (6), 773−778.
(24) Sui, Q.; Huang, J.; Deng, S.; Chen, W.; Yu, G. Seasonal Variation in the Occurrence and Removal of Pharmaceuticals and Personal Care Products in Different Biological Wastewater Treatment Processes. *Environ. Sci. Technol.* **2011**, *45* (8), 3341−3348.
(25) Sui, Q.; Huang, J.; Deng, S.; Yu, G.; Fan, Q. Occurrence and removal of pharmaceuticals, caffeine and DEET in wastewater treatment plants of Beijing, China. *Water Res.* **2010**, *44* (2), 417−426.
(26) Gao, L.; Shi, Y.; Li, W.; Liu, J.; Cai, Y. Occurrence, distribution and bioaccumulation of antibiotics in the Haihe River in China. *J. Environ. Monit.* **2012**, *14* (4), 1248−1255.
(27) China Meteorological Data Sharing Sevice System. http://cdc.cma.gov.cn. Accessed 9/19/2011.
(28) Shi, Y.; Xiao, J.; Shen, Y. Landscape Pattern Change and Associated Environmental Implications in the Haihe River Basin, China. *Int. Arch. Photogramm, Remote Sens. Spatial Inf. Sci.* **2008**, *37*, (B4).
(29) Shah, T.; Roy, A. D.; Qureshi, A. S.; Wang, J. Sustaining Asia's groundwater boom: An overview of issues and evidence. *Nat. Resour. Forum* **2003**, *27* (2), 130−141.
(30) Kern, S.; Fenner, K.; Singer, H. P.; Schwarzenbach, R. P.; Hollender, J. Identification of Transformation Products of Organic Contaminants in Natural Waters by Computer-Aided Prediction and High-Resolution Mass Spectrometry. *Environ. Sci. Technol.* **2009**, *43* (18), 7039−7046.
(31) Singer, H.; Longrée, P.; Goetz, C.; Abegglen, C. *Screening-Messungen von organischen Mikroverunreinigungen im Bodensee. Substanzinventarisierung für das Freiwasser*; Swiss Federal Institute of Aquatic Science and Technology: Duebendorf, Switzerland, 2009.
(32) National Bureau of Statistics. *Statistical Yearbook of Chinese Medicine*; Beijing, China, 2009.
(33) National Bureau of Statistics. *Statistical Yearbook of Chinese Pesticides*; Beijing, China, 2009.
(34) Stoob, K.; Singer, H.; Goetz, C.; Ruff, M.; Mueller, S. Fully automated online solid phase extraction coupled directly to liquid chromatography−tandem mass spectrometry. Quantification of sulfonamide antibiotics, neutral and acidic pesticides at low concentrations in surface waters. *J. Chromatogr., A* **2005**, *1097* (1−2), 138−147.
(35) Singer, H.; Jaus, S.; Hanke, I.; Lück, A.; Hollender, J.; Alder, A. C. Determination of biocides and pesticides by on-line solid phase extraction coupled with mass spectrometry and their behaviour in wastewater and surface water. *Environ. Pollut.* **2010**, *158* (10), 3054−3064.
(36) Kolpin, D. W.; Furlong, E. T.; Meyer, M. T.; Thurman, E. M.; Zaugg, S. D.; Barber, L. B.; Buxton, H. T. Pharmaceuticals, Hormones, and Other Organic Wastewater Contaminants in U.S. Streams, 1999−2000: A National Reconnaissance. *Environ. Sci. Technol.* **2002**, *36* (6), 1202−1211.
(37) Research and Markets, Production and Market of Sucralose in China. http://www.researchandmarkets.com/research/08250a/production_and_market_of_sucralose_in_china. Accessed 9/19/2011.
(38) Wick, A. Occurrence and fate of emerging organic micropollutants in biological wastewater treatment. Ph.D. Dissertation, Universität Koblenz-Landau, Koblenz, Germany, 2011.
(39) European Parliament and Council Directive 2008/105/EC. 2008.
(40) *European Union Technical Guidance for Deriving Environmental Quality Standards. Common Implementation Strategy for the Water Framework Directive 2000/60/EC.* In 2010; Vol. WG E(9)-10-03e-TGD-EQS (final draft).
(41) Junghans, M.; Chèvre, N.; Di Paolo, C.; Eggen, R. I. L.; Gälli, R.; Gregorio, V.; Häner, A.; Homazava, N.; Perazzolo, C.; Kase, R. *Aquatic Risks of Plant Protection Products: A Comparison of Different Hazard Assessment Strategies for Surface Waters in Switzerland*; Study on behalf

of the Swiss Federal Office for the Environment; Swiss Centre for Applied Ecotoxicology: Duebendorf, Switzerland, 2011.
(42) Swiss Centre for Applied Ecotoxicology. Qualitätskriterien für organische Spurenstoffe in Oberflächengewässern. http://www.oekotoxzentrum.ch/expertenservice/qualitaetskriterien/index. Accessed 7/18/2011.
(43) Posthuma-Doodeman, C. J. A. M. *Environmental Risk Limits for Imidacolprid*; National Institute for Public Health and the Environment: Bilthoven, the Netherlands, 2008.
(44) Altenburger, R.; Walter, H.; Grote, M. What Contributes to the Combined Effect of a Complex Mixture? *Environ. Sci. Technol.* **2004**, *38* (23), 6353−6362.
(45) Buerge, I. J.; Poiger, T.; Müller, M. D.; Buser, H.-R. Caffeine, an Anthropogenic Marker for Wastewater Contamination of Surface Waters. *Environ. Sci. Technol.* **2003**, *37* (4), 691−700.
(46) Weissbrodt, D.; Kovalova, L.; Ort, C.; Pazhepurackel, V.; Moser, R.; Hollender, J.; Siegrist, H.; McArdell, C. S. Mass flows of X-ray Contrast Media and Cytostatics in Hospital Wastewater. *Environ. Sci. Technol.* **2009**, *43* (13), 4810−4817.
(47) Götz, C. W.; Kase, R.; Hollender, J. *Mikroverunreinigungen - Beurteilungskonzept für organische Spurenstoffe aus kommunalem Abwasser. Studie im Auftrag des BAFU*; Swiss Federal Institute of Aquatic Science and Technology: Duebendorf, Switzerland, 2011.
(48) Campbell, C.; Chui, M. *Pharmerging Shake-Up*; IMS Health: Norwalk, USA, 2010.
(49) Fatta-Kassinos, D.; Meric, S.; Nikolaou, A. Pharmaceutical residues in environmental waters and wastewater: current state of knowledge and future research. *Anal. Bioanal. Chem.* **2010**, *399* (1), 251−275.
(50) Hernández-Leal, L.; Temmink, H.; Zeeman, G.; Buisman, C. J. N. Removal of micropollutants from aerobically treated grey water via ozone and activated carbon. *Water Res.* **2011**, *45* (9), 2887−2896.
(51) Zhou, J.; Liu, P.; Li, K.; Gan, Y. *Beijing Municipal Wastewater Treatment and Reuse Analysis and Development*; China Environment Chamber of Commerce: Beijing, China, 2011.
(52) Voutsa, D.; Hartmann, P.; Schaffner, C.; Giger, W. Benzotriazoles, Alkylphenols and Bisphenol A in Municipal Wastewaters and in the Glatt River, Switzerland. *Environ. Sci. Pollut. Res.* **2006**, *13* (5), 333−341.
(53) Reemtsma, T.; Miehe, U.; Duennbier, U.; Jekel, M. Polar pollutants in municipal wastewater and the water cycle: Occurrence and removal of benzotriazoles. *Water Res.* **2010**, *44* (2), 596−604.
(54) Giger, W.; Schaffner, C.; Kohler, H.-P. E. Benzotriazole and Tolyltriazole as Aquatic Contaminants. 1. Input and Occurrence in Rivers and Lakes. *Environ. Sci. Technol.* **2006**, *40* (23), 7186−7192.
(55) Janna, H.; Scrimshaw, M. D.; Williams, R. J.; Churchley, J.; Sumpter, J. P. From Dishwasher to Tap? Xenobiotic Substances Benzotriazole and Tolyltriazole in the Environment. *Environ. Sci. Technol.* **2011**, *45* (9), 3858−3864.
(56) Fang, S.-B.; Hu, H.; Sun, W.-C.; Pan, J.-J. Spatial Variations of Heavy Metals in the Soils of Vegetable-Growing Land along Urban-Rural Gradient of Nanjing, China. *Int. J. Environ. Res. Public Health* **2011**, *8* (6), 1805−1816.
(57) Wittmer, I. K.; Scheidegger, R.; Bader, H.-P.; Singer, H.; Stamm, C. Loss rates of urban biocides can exceed those of agricultural pesticides. *Sci. Total Environ.* **2011**, *409* (5), 920−932.
(58) Kendy, E.; Gérard-Marchant, P.; Todd Walter, M.; Zhang, Y.; Liu, C.; Steenhuis, T. S. A soil-water-balance approach to quantify groundwater recharge from irrigated cropland in the North China Plain. *Hydrol. Process.* **2003**, *17* (10), 2011−2031.
(59) Kendy, E.; Zhang, Y.; Liu, C.; Wang, J.; Steenhuis, T. Groundwater recharge from irrigated cropland in the North China Plain: case study of Luancheng County, Hebei Province, 1949−2000. *Hydrol. Process.* **2004**, *18* (12), 2289−2302.
(60) von Rohden, C.; Kreuzer, A.; Chen, Z.; Kipfer, R.; Aeschbach-Hertig, W. Characterizing the recharge regime of the strongly exploited aquifers of the North China Plain by environmental tracers. *Water Resour. Res.* **2010**, *46* (5), W05511.
(61) Kazner, C., Wintgens, T., Dillon, P., Eds. *Water Reclamation Technologies for Safe Managed Aquifer Recharge*; IWA Publishing: London, UK, 2012.
(62) Siemens, J.; Huschek, G.; Walshe, G.; Siebe, C.; Kasteel, R.; Wulf, S.; Clemens, J.; Kaupenjohann, M. Transport of Pharmaceuticals in Columns of a Wastewater-Irrigated Mexican Clay Soil. *J. Environ. Qual.* **2010**, *39* (4), 1201−1210.
(63) Cordy, G. E.; Duran, N. L.; Bouwer, H.; Rice, R. C.; Furlong, E. T.; Zaugg, S. D.; Meyer, M. T.; Barber, L. B.; Kolpin, D. W. Do Pharmaceuticals, Pathogens, and Other Organic Waste Water Compounds Persist When Waste Water Is Used for Recharge? *Ground Water Monit. Rem.* **2004**, *24* (2), 58−69.
(64) McKinsey Global Institute. *Preparing for China's urban billion. Impacts of urbanization: Implications for urban water*; 2009.
(65) Vorosmarty, C. J.; Green, P.; Salisbury, J.; Lammers, R. B. Global Water Resources: Vulnerability from Climate Change and Population Growth. *Science* **2000**, *289* (5477), 284−288.