Application of the GREAT-ER model for environmental risk assessment of nonylphenol and nonylphenol ethoxylates in China

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Abstract The environmental risk presented by “down-the-drain” chemicals to receiving rivers in large urban areas has received increasing attention in recent years. Geo-referenced Regional Environmental Assessment Tool for European Rivers (GREAT-ER) is a typical river catchment model that has been specifically developed for the risk assessment of these chemicals and applied in many European rivers. By utilizing the new version of the model, GREAT-ER 3.0, which is the first completely open source software for worldwide application, this study represents the first attempt to conduct an application of GREAT-ER in the Wenyu River of China. Aquatic exposure simulation and an environmental risk assessment of nonylphenol (NP) and its environmental precursor nonylphenol ethoxylates (NPEOs) were conducted effectively by GREAT-ER model, since NP is one of typical endocrine disrupting chemicals (EDCs) and its environmental precursor NPEOs as a “down-the-drain” chemical are extensively used

in China. In the result, the predicted environmental concentrations (PECs) of NP and NPEOs in the water of Wenyu River were 538 and 4320 ng/L, respectively, at the regional scale, and 1210 and 8990 ng/L, respectively, at the local scale. From the results profile of the RCR, the combination of high emissions from large STPs with insufficient dilution of the river caused the high RCR. The PECs of NP in the sediment were in the range of 216.8–8218.3 ng/g (dry weight), which was consistent with the available monitoring data. The study showed the worldwide applicability and reliability of GREAT-ER as a river catchment model for the risk assessment of these chemicals and also revealed the general environmental risks presented by NP and NPEOs in the Wenyu River catchment in Beijing due to the extensive use of these chemicals. The results suggest that specific control or treatment measures are probably warranted for these chemicals to reduce their discharge in major cities.

Keywords “Down-the-drain” chemicals · Risk assessment · GREAT-ER · Catchment establishment · NP and NPEOs

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Introduction

The environmental risks of “down-the-drain” chemicals, which are usually caused by their use in various industrial or household chemical products and the subsequent discharge into rivers via sewage treatment plants (STPs) in urban areas, have attracted increasing attention in recent years (Diamanti-Kandarakis et al. 2009; Kavlock et al. 1996; Keller 2006; Koormann et al. 2006; USEPA 2006). Especially, a part of “down-the-drain” chemicals such as phthalates (PAEs), bisphenol A (BPA), and nonylphenol (NP) is considered to be endocrine disrupting chemicals (EDCs) (EU 2008; USEPA 2006; An and Hu 2006; Welshons et al. 2003). The use of

nonylphenol and nonylphenol ethoxylates has been severely restricted in developed countries, but they are still widely used in China. Nonylphenol is present in high concentrations in the aquatic environment in China. Numerous monitoring studies have indicated that contamination levels of NP and NPEOs (In this paper, the term “NP and NPEOs” represents a series of isomeric compounds of nonylphenol and nonylphenol ethoxylates, a term incorporating a number of chemically different compounds) have reached 1000 ng/L in rivers and are as high as 7000 ng/g in sediments in major industrialized urban areas of China, which represent a relatively high aquatic environmental exposure level (Chen et al. 2006; Fu et al. 2008; Hou et al. 2005; Shao et al. 2002; Wang et al. 2010; Xu et al. 2006; Yu et al. 2008; Zhao et al. 2009). However, most of these were conducted using a monitoring methodology, which may not reflect typical or average concentrations, since the chemical analyses are limited by the spatial and temporal resolutions of sampling. In contrast, modeled concentrations generally reflect typical or average concentrations required for detailed environmental risk assessment (Leeuwen and Vermeire 2007). To assess the environmental risks of “down-the-drain” chemicals in rivers, GREAT-ER has proven to be a well-developed and reliable model that simulates environmental concentrations and provides risk distributions of these chemicals in a series of individual European catchments (Cunningham et al. 2010; Hannah et al. 2009; Hüffmeyer et al. 2009; Sabaliunas et al. 2003). By establishing a European digital river network based on input data including hydrological data, emission information, and other parameters, GREAT-ER has been successfully used to simulate environmental concentrations and assess the environmental risks of surfactants such as alkylbenzene sulfonate (Fox et al. 2000), drugs such as ethinyl estradiol and aspirin (Schowanek and Webb 2002), and EDCs such as estradiol and estrogen estrone (Sabaliunas et al. 2003; Sumpter et al. 2006). GREAT-ER is also used to simulate emerging contaminants diclofenac in Spain recently (Aldekoa et al. 2013). In 2012, a new version of the model with the first open source software for a river catchment self-establishment was published (i.e., GREAT-ER 3.0), providing a valuable opportunity and technical support for its worldwide application (Schowanek et al. 2012). New version of the GREAT-ER software is applied for the prediction of spatially explicit exposure concentrations of pharmaceutical diclofenac in Germany (Kehrein et al. 2015).

In this study, the use of the GREAT-ER model is introduced to a Chinese environment, to conduct a practical environmental risk assessment of NP and its environmental precursor NPEOs in the Wenyu River catchment in Beijing, China. The catchment is typical receiving water for “down-the-drain” chemicals, and NP and NPEO monitoring data have been obtained for this environment; however, no environmental risk assessment of the river catchment has been undertaken.

Materials and methods

NP and NPEOs

In this study, the term “NP” denotes a mixture of various isomers of nonylphenol, predominantly para-substituted nonylphenol, with small amounts of ortho-substituted phenol and 2,4-dinonylphenol, which represent numerous branched structures that occur within the nine-carbon group. The final technical mixtures of NP contain more than 22 isomers of 4-substituted monoalkylphenols (Thiele et al. 2004; Wheeler et al. 1997).

NP is mainly used as an intermediate for the production of NPEOs which are nonionic surfactants widely used in industrial and household detergents, cleaning agents, emulsifiers, and dispersing agents (An and Hu 2006). The term “NPEOs” denotes a mixture of compounds with different chain ethoxylation of nonylphenol, which contains an ethoxylate chain with a recalcitrance that increases with decreasing number of ethoxylate groups. Under ambient conditions, numerous NPs can be obtained from the breakdown of NPEOs, which is the main source of NP contamination. NP is a well-known EDC, which interferes with the hormonal and endocrine systems of organisms. Although the NP isomers in technical NP mixtures may differ in the strength of their endocrine activity (Preuss et al. 2006), the model applied here was simplified by assuming that they had approximately equivalent endocrine activity, and the sum of concentrations of NP isomers was used to indicate the environmental risk of this kind of EDC.

Model and target catchment

A schematic diagram of the GREAT-ER modeling in our study is shown in Fig. 1, which is based on Boeije (1999) and Feijtel et al. (1997), indicating the modeling processes and relevant key parameters in the study. First, a river catchment for simulation of the emission and distribution of “down-the-drain” chemicals needs to be established, which can also be used for other similar chemicals. This requires not only a collection of geographic data which based on geographic information system (GIS) and hydrologic information with flow volume, flow velocity, and latitude/longitude coordinates of each segment for the river catchment, but also population data received by STP and types, coordinates, sewage treatment capacity, and removal of the STPs in the catchment. A practical modeling scenario for the target “down-the-drain” chemicals can be built according to their emission inventory, the removal rate of the chemicals by STPs, and the migration and transformation rates in the river. Finally, the concentrations of the targeted “down-the-drain” chemicals in the water and sediment of the river catchment and the environmental risk implications are derived by the modeling.

Fig. 1 The GREAT-ER modelling processes in the study

The Wenyu River catchment was selected for this GREAT-ER modeling study. The Wenyu River catchment is located in the northeast of Beijing, as shown in Fig. 2. Fundamental and general information about the catchment area, the main streams and tributaries, the total sewage discharge, and sewage treatment works are provided in the supporting information. The Wenyu River flows through the northern and eastern

regions of Beijing, through a high density of residential and industrial areas, and is a significant receiving water for “down-the-drain” chemicals in this urban area (Zheng et al. 2007). The information and parameters required to construct a GREAT-ER model for this catchment can be easily obtained, and hence, the Wenyu River may be selected as an ideal site for study of NP and NPEOs (Lei et al. 2008a, b).

Fig. 2 The digital network map of the Wenyu River catchment that was built for GREAT-ER

Catchment establishment for modeling

The building of a catchment of the local river for GREAT-ER modeling is a fundamental part of this study. First, we built a digital network map of the Wenyu River catchment in Beijing based on the digital elevation model (DEM) map and GIS simulation (Fig. 2) in which flow direction corrections were made for each river segment according to the actual situation. Second, the river segments in this catchment were coded with numbers from 1 to 40 shown in Fig. 2, and normal stream flows for each river segment were obtained from hydrological monitoring data. However, in this case, the current hydrological monitoring data for the Wenyu River catchment were insufficient for generating detailed stream flows of the river, and instead, Soil and Water Assessment Tool (SWAT; Arnold et al. 2012), a hydrology and water quality model, was used to simulate stream flows of each river segment in the catchment. The SWAT simulation results on flow volumes have been well validated with onsite monitoring data (Tang et al. 2010; Zhang et al. 2009). In practice, stream flow values of the river for modeling were obtained based on the results of simulated outlet flows for each segment by SWAT, following the necessary data transformation and correction (hydrologic information of these 40 segments were shown in Table S1 in supporting information). Certain other catchment establishment data, such as flow rates and river depths, were calculated by empirical formulas contained in the modules of GREAT-ER itself.

The third important part is the correct assignment of STPs to the respective river segments. Because “down-the-drain” chemicals are released to the aquatic environment through STPs from household and industrial processes, STPs were selected as point sources of these chemicals in this study. Information regarding STPs in the Wenyu River catchment was collected based on field research and expert inquiry, and mainly included the location of STPs, the population served, sewage flow, and operating conditions. Eleven STPs with large discharge volumes that flow into the Wenyu River catchment were selected as point sources for the catchment building phase of the study; the discharge volume from these forms 93 % of the total discharge and most emissions of “down-the-drain” chemical can be accounted for by considering these 11 STPs. The location, daily wastewater flow, and STP treatment type of each STP are shown in Table S2 (Supporting Information).

Simulation scenario building

Estimation of the emission of NP and NPEOs within the catchment

NP (the physicochemical properties and introduction were shown in supporting information) is not only an industrial

intermediate for NPEOs but also a metabolite of nonylphenol ethoxylates (NPEOs) in the aquatic environment. Under environmental and STP conditions, long-chain NPEOs will break down to NP, nonylphenol monoethoxylate (NPEO₁) and nonylphenol diethoxylate (NPEO₂), and other metabolites. In this paper, the emission of NPs is considered from two sources: NPEO degradation from industrial and household use and NPEO breakdown under STP conditions. NP concentrations are then used as a direct and easily measurable indicator in the risk assessment.

According to our survey on NP and NPEOs industrial sources in Beijing area, there were no industrial sources of NP and NPEOs in our studying area and the only few industrial sources all located at the southeast edge zone of Beijing, which is almost the downstream end of the Wenyu River and out of our studying areas. Then, the residential emission through STPs is the dominant source of NP and NPEOs in the Wenyu River catchment in the study. Because more than 95 % of all wastewater in Beijing is treated, the NP and NPEOs used in this area were all assumed to have been processed by a STP, and that fugitive emissions of NP and NPEOs could be neglected. According to the GREAT-ER model, the per capita chemical consumption (PCC) of NP and NPEOs in the Wenyu River catchment needs to be estimated to simulate their emission from STPs. Given that there is no statistical information about NP and NPEOs consumption in the target area, a practical method based on the monitored STP influent concentration ranges of NP and NPEOs, total influent flows per year for each STP, and the population served by the STPs was adopted to estimate the PCCs of NP and NPEOs (Balaam et al. 2010; Whelan et al. 2012), which can be calculated by the following equation:

$$PCC = \frac{C_{inf} \cdot M \cdot Q_{inf}}{P} \quad (1)$$

where PCC is the annual per capita emission (kg/cap/year), C_{inf} is the STP influent concentration (mol/L) for each point source, M is the molecular weight (g/mol) for NP and NPEOs in this study, Q_{inf} is the STP influent volume (m³/day), and P is the population served by the STP (cap).

The influent concentration of NP only represents emission from NPEOs degradation used as a surfactant and that of NPEOs stands for the emission without degradation into the STP. According to the monitoring data, the observed NP and NPEOs influent concentration in four major STPs of the Wenyu River catchment were in range of 0.028~0.095 µmol/L for NP and 0.116~0.365 µmol/L for NPEOs (Hao et al. 2007; Hou and Sun 2006; Lian et al. 2009). Average concentrations of NP and NPEOs of these four major

STPs were used to calculate their PCCs by equation (1) according to an investigation of the influent volume and population served of the STPs in the Wenyu River catchment (shown in the Table S2 in supporting information). Average PCC values of NP and NPEO were $(5.73 \pm 1.62) \times 10^{-4}$ kg/cap/year and $(4.24 \pm 0.47) \times 10^{-3}$ kg/cap/year, respectively. In the simulations, these average values were used as constant input for all STPs.

NP and NPEOs removal by STPs

The part is on the STP removal of NP and NPEOs during the sewage treatment. The NP and NPEOs removal rates by STPs are a basic parameters required to model their distribution by GREAT-ER. Many studies of the fate and degradation of NP and NPEOs in STPs in China are available, but a study conducted by Lian et al. (2009) in four types of STPs in Beijing provides the most relevant references for our study. In Lian et al. (2009) study, the removal rates of NP and NPEOs in STPs were investigated in four STPs that used different types of treatment processes, with a biomembrane and an oxidation ditch. The average influent and effluent concentration of NP in activated sludge (AS) is 0.034 and 0.001 $\mu\text{mol/L}$, respectively. Also in the trickling filter (TF), the average influent and effluent concentration of NP is 0.062 and 0.001 $\mu\text{mol/L}$, respectively. The total removal rate of NP in activated sludge is 97.1 % and in the trickling filter is 98.4 %. The individual removal rates of NP and NPEOs during sewage treatment must be considered separately. According to Lian et al (2009), the NPEOs concentration is 0.149 and 0.019 $\mu\text{mol/L}$ in the inlet and outlet of activated sludge, and 0.308 and 0.030 $\mu\text{mol/L}$ for the trickling filter, respectively. The NPEO removal rate in the AS and TF can be considered to be 87.2 and 90.2 %.

Removal of NP and NPEOs in rivers and sediment

After the STP removal of NP and NPEOs during the sewage treatment, the removal rate of NP and NPEOs in the aquatic environment of the river is another key factor for the simulation of their concentration and distribution in the environment. Generally, the in-river removal processes of NP and NPEOs should comply with first-order kinetics. Sundaram and Szeto (1981) indicated that the half-life of NP in a river was about 2.5–16.5 days in a study based on the open environment and experimental conditions. Other studies have also concluded that the half-life of NP in surface water ranges from 8.5 to 30 days (Nielsen et al. 1999; Sumpter et al. 2006). Based on the relationship between half-life and the first-order reaction rate shown in Eq. (2), and also taking into account volatilization, sedimentation, and degradation processes, the in-

river removal rate of NP was inferred as 0.0034–0.0115/h using the following formula,

$$k = \frac{\ln 2}{HL} \quad (2)$$

where HL is the half-life of chemicals (h) and k is the first-order reaction rate (/h). In a river environment, NPEOs have a higher degradation and removal rate than NP, with a half-life of about 4.5 days (Yoshimura 1986). Ahel et al. (1994) reported that removal rates of NPEOs were 0.0145–0.0154/h in high flow velocity and 0.0096/h in low flow velocity. Tong and Nie (2011) concluded that the removal rate of NPEOs in rivers was about 0.0103/h. Considering the similarity of these locations to the Wenyu River, these in-river removal rates of NPEOs were used in this study.

In the sediment extension module of GREAT-ER model, the sediment concentration of NP can be affected by dissolved concentration in river. The equilibrium can be used as (3)

$$C_{\text{sediment}} = f_d \cdot C_{\text{total}} \cdot K_{\text{SW}} = C_{\text{dissolved}} \cdot \left(K_{\text{d_river}} \frac{\rho_s}{\rho_w} \right)$$

where ρ^s is 1300 kg/d.w./l for dry sediment density; ρ_w is 1 kg/L for water density; and θ is 0.8 for volumetric water fraction of the sediment. The value of $K_{\text{d_river}}$ is from the output of the GREAT-ER water model.

(Main parameters used for NP and NPEOs for simulation can be found at Table S4 in supporting information).

Results and discussion

Simulation results and verification

The distribution of NP in the Wenyu River catchment as simulated by GREAT-ER is shown in Fig. 3. The concentration of NP was predicted to be about 538 ng/L at the regional scale, giving the average of representative concentrations over all catchment segments. The concentration of NP in each stream segment was affected by the location of major STPs throughout the catchment and ranged from dozens to several thousands of nanogram per liter. To show the distribution of NP concentrations, the concentration scales were classified into seven levels, shown in Fig. 3. The concentrations of NP were predicted to be high in the streams close to the outlets of the major STPs, and then to decrease downstream due to the processes of migration and transformation processes in the river. The predicted concentration of NP at the outlets of the 11 STPs averaged 1210 ng/L at the local scale, which can be defined as the mean of all concentrations at the beginning of a river stretch directly receiving a treated or untreated waste water emission.

Fig. 3 Distribution of NP in the Wenyu River catchment in Beijing

According to the simulation results, downstream of the Beisha River, middle stream and downstream of the Qing River, and the Ba River segment contained high concentrations of NP (1500 ng/L in some river segments) because these

segments contained the major municipal STPs within the catchment that serve a large population and have a large daily treatment capacity. The NP concentration in the segment of the upstream Sha River Gate was lower than 110 ng/L, which

Fig. 4 Comparison of the simulated and measured concentrations of NP in mainstream sediments of the Wenyu River

can be explained by the high flow rate of the river generated by the impounding dam there. There is a concentration drop after emission from STP 5. The concentration of NP from STP 5 is lower than that in the segment 25 which is the upstream. The NP concentration was lower than 250 ng/L in upstream from the Sha River Gate to the Qing River junction, while it was higher than 700 ng/L from the confluence of the Qing River and the mainstream to upstream Beiguan Gate, showing the distribution of high NP pollution levels in the catchment.

Simulation results predicted an environmental NPEOs concentration of 4320 ng/L at the regional scale and 8990 ng/L at the local scale. Studies have shown that long-chain NPEOs degrade into short-chain chemicals, such as NP₁EO and NP₂EO in water and sediments, and those parts of them can be transformed into NP. Taking into account the transformation processes of long- to short-chain NPEOs in STPs, this proportion of short-chain NPEOs could increase further. The relationship between NP and NPEOs after sewage treatment

processes should be considered; the NPEOs break down to NP and short-chain NPEOs under anoxic and aerobic conditions, and the actual NP concentration will be higher than the simulated concentration. However, the quantitative relation between increasing NP concentrations and decreasing NPEO concentrations is not simple to evaluate and simulate. With the removal of NPEOs from rivers and sediments, NP concentrations will continue to increase.

While the monitoring studies of NP in streams of the Wenyu River catchment are lacking, monitoring studies of NP in the sediment of this river catchment are available and have provided a database that can be used for the validation of our modeling results. A monitoring study of NP in sediments at 10 sites along the Wenyu River, from upstream of the Sha River Gate to Beiguan Gate, indicated that the NP concentration in the sediment was in the range of 124.5–8157.9 ng/g (dry weight, d.w.; Lei et al. 2008a). The predicted concentration of NP in sediment by GREAT-ER was in the range of

Fig. 5 Environmental risk profile of NP in the surface water (a) and sediment (b) in the Wenyu River catchment (river segments in red indicate an RCR greater than 1; river segments in green indicate an RCR less than 1)

216.8–8218.3 ng/g (d.w.), which indicated a general compatibility between the modeling and monitoring results. A detailed comparison of the modeling and monitoring results of the NP concentration in the sediment among the 10 sites selected for monitoring is shown in Fig. 4. Linear regression analysis has been performed on the results of modeling and monitoring, and the correlation coefficient (R^2) was found to be 0.94, indicating a high level of consistency between the modeling and monitoring results. The model predicted concentrations at most sites in upstream sectors of the river that were higher than the values obtained by monitoring, which could be attributable to the difficulties that the model experienced in reflecting the dilution effect caused by the impoundment of the Sha River Reservoir. Nevertheless, the data point at 20.5 km is abnormal because the monitoring data were 10 times more than that by the model. Further exploration showed that there is an unreasonable discharge outlet, rather than a STP, which lead to high concentration of NP. In downstream sectors of the Wenyu River, both monitoring and modeling concentrations showed a sharp increase of NP concentrations in sediments, with a maximum value of 8157.9 and 8218.3 ng/g (d.w.), respectively, indicating serious pollution of NP in downstream sectors of the river.

Risk analysis

In this study, the risk characterization ratio (RCR; i.e., the ratio of the PEC and predicted no-effect concentration, PNEC) was used to characterize the risk profile of NP in water and sediments in the Wenyu River catchment. According to a number of ecotoxicological studies undertaken in the European Union, the PNEC of NP is about 330 ng/L in water and 39 ng/g (d.w.) in sediment (EU 2002). Figure 5 shows the environmental risk profile of NP in the surface water and sediment throughout in the Wenyu River catchment. The high RCR of NP in water generally occurs in river segments containing major STPs that serve highly industrialized and populated zones. Consequently, environmental risks are mainly presented in the upstream Shahe Reservoir, downstream Beisha River and Dongsha River, and Qing River, Ba River, and downstream Wenyu River segments. These results indicate that large STPs could generate local aquatic environmental risks from “down-the-drain” chemicals such as NP.

According to risk situation of NP in sediments, without considering background concentrations, the RCR value for NP was greater than 1 in the sediment in all river segments downstream of STPs, indicating high environmental risks due to NP in the sediment in the Wenyu River catchment. The difference RCRs of each segment between in river and in sediment is due to the respective PNEC of NP, which indicated a potential risk level in this aquatic environment.

Although the simulation results of NP risk in the target catchment are reasonable and verifiable, a number of

uncertainty factors may lead to inaccurate simulation results. Firstly, the limited and singular database providing information on hydrology, population, STPs in the target catchment, and the physicochemical properties and removal rate in STPs and rivers of NP and NPEOs provides the most significant source of uncertainties in this research. Secondly, the NP-simulated environmental risk did not include NPEOs breakdown after emission from an STP, in rivers and sediment, and is likely an underestimate. Some localized parameters for the GREAT-ER model are also lacking which is likely to impact the results. Overall, the development of a more accurate risk assessment in China using the GREAT-ER model may require further study.

Conclusion

The study realized the first application of GREAT-ER as a European river catchment model for the risk assessment of “down-the-drain” chemicals in a river of China, indicating the worldwide applicability and reliability of this model. The model simulation revealed the general environmental risks presented by NP and NPEOs in the Wenyu River catchment in Beijing due to the extensive use of these chemicals, which implied the specific control or treatment measures are needed to reduce emissions of those EDCs chemicals in major cities. While the approach in this study can be an effective and applicable way to simulate chemicals in aquatic environment in the poor-data region, many aspects supporting a more precise simulation need to be developed especially including statistic data on regional chemicals consumption, more precise geographic and hydrological information of the rivers and more representative monitoring data of chemicals of concern.

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- The English in the revised manuscript has been checked again by at least two professional editors, both native speakers of English. For a certificate, please see: <http://www.textcheck.com/certificate/Jx02ej>.