Emerging Contaminants 2 (2016) 148–156

Contents lists available at ScienceDirect

Emerging Contaminants

journal homepage: http://www.keaipublishing.com/en/journals/emerging-contaminants/

Discharge inventory of pharmaceuticals and personal care products in Beijing, China

Zhixia Zhang [a, b], Bin Wang [a, c, *], Honglin Yuan [b], Ruixue Ma [a, c], Jun Huang [a, c], Shubo Deng [a, c], Yujue Wang [a, c], Gang Yu [a, c]

[a] Beijing Key Laboratory of Emerging Organic Contaminants Control, State Key Joint Laboratory of Environmental Simulation and Pollution Control, School of Environment, Tsinghua University, Beijing, 100084, China

[b] School of Environmental and Municipal Engineering, Xi'an University of Architecture and Technology, Xi'an, 710055, China

[c] Collaborative Innovation Center for Regional Environmental Quality, Tsinghua University, Beijing, 100084, China

A R T I C L E I N F O

Article history:
Received 1 April 2016
Received in revised form 18 July 2016
Accepted 19 July 2016
Available online 27 July 2016

Keywords:
Pharmaceuticals and personal care products (PPCPs)
Discharge inventory
Pollution sources
Beijing

A B S T R A C T

Pharmaceuticals and personal care products (PPCPs) are emerging environmental contaminants, whose potential risk for the ecological environment has caused wide attention in recent years. In China, quite a large amount of PPCPs were annually emitted into the environment. Their existence in different matrix has been reported frequently, including river water, sediment and soil. However, the contribution from different sources was seldom reported and still unclear in China. Wastewater treatment plant (WWTP) was usually considered to be the main source to the urban river, but livestock and aquaculture farms were also reported as significant pollution sources of PPCPs due to poor environmental management in China. This study summarized environmental discharges of different PPCPs from various sources and obtained the discharge data through different environment media in Beijing, the statistical source of PPCPs was analyzed in detail. The sources comprised WWTPs, excess sludge, hospital wastewater, municipal untreated wastewater, aquaculture wastewater and landfill leachate. This article helps understand the general situation and the potential risk of PPCPs in Beijing.

1. Introduction

Pharmaceuticals and personal care products (PPCPs) are used to treat or prevent human and animal disease and improve the quality of daily life [1,2]. Human-use PPCPs are mainly emitted into WWTPs and finally enter the surface water, as the effluent is used for irrigation and sludge is applied in agriculture as fertilizer [3,4]. Veterinary pharmaceuticals tend to be released to aquaculture directly and after usage in livestock, it may indirectly pollute groundwater during the land application of manure and slurry in livestock [5]. PPCPs may also be released to the aquatic environment from manufacturing sites.

China produces and consumes a large amount of PPCPs every year and a substantial amount of work has been done by the scientists as it has been reported frequently in different media with significant concentration and potential effect on human and environment [2,6–9]. They may also cause persistent contamination due to continuous discharge [4,10].

As emerging contaminants, PPCPs has currently become one of hotspots in environmental research [11–14]. However, the contribution, transport and fate of PPCPs in different environmental media and sources is unclear, which leads to an absence of comprehensive information to grasp the overall pollution situation [8,15–17]. Previous studies indicated that WWTP was the dominant PPCPs source to aquatic environment [18–21]. But other sources may contribute more in some cases [22]. Usually, the effluents from wastewater enhance the levels of pollutants, but it was shown in a research that the surface water concentration was significantly diluted by WWTPs effluent [23], the high concentration suggested there may be other point or non-point PPCPs sources existed.

* Corresponding author. School of Environment, Tsinghua University, Beijing, 100084, China.
E-mail address: thuwb@tsinghua.edu.cn (B. Wang).
Peer review under responsibility of KeAi Communications Co., Ltd.

http://dx.doi.org/10.1016/j.emcon.2016.07.001

As the Chinese political and culture communication center, Beijing has developed rapidly in recent decades. With the increase of population and urbanization under speedy economic growth, many public problems such as 'City disease' as well as environmental pollution in megacity was prevalent [24]. The municipal utilities and public service facilities constructed previously could not meet the cities' requirement yet. The drainage pipeline system was mainly built in eighties and ninties of the 20th century, which does not cover the municipal network completely [25,26]. Currently, the water treatment capacity is 1.37 billion tons, far less than the total wastewater volume discharged in Beijing, which implies quite a proportion of untreated wastewater. It was reported, seven discharge outlets along the Liangshui River discharged 60,000 tons of untreated wastewater per day into the river (http://green.sohu.com/20130822/n384773793.shtml). The pollution was frequently reported, as high concentration in surface water and sewage was significantly related with livestock where PPCPs was polluted seriously (from ng/L to ug/L) [9,18,27]. Caffeine concentration in Beijing surface water was up to 4200 ng/L and the popular bug repellent DEET (N,N-Diethyl-3-methyl benzoyl amide) was 546 ng/L in summer [28,29].

For the issue above, we identified key PPCPs sources and surveyed their pollution status and contribution through literature research and statistical analysis. The sources include influent, effluent and sludge in WWTPs, untreated municipal wastewater, hospital wastewater, aquaculture wastewater, livestock excretion (dung and urine) and leachate in municipal landfill. The article established a comprehensive PPCPs' discharge inventory from multiple pollution sources and provided a scientific basis for environmental management of such PPCPs in Beijing.

2. Materials and methods

The investigation method of PPCPs contamination is shown in Fig. 1. The research launched the investigation through official statistics from official website database and statistics in literature. Original statistics mainly comprise PPCPs concentration data in different sources, parameter statistics include discharge coefficient and emission quantity from all the sources.

Recently, researchers mainly focused on the PPCPs contamination related to wastewater in WWTPs. PPCPs discharge was classified into two categories: liquid sewage poured into aquatic environment including resident sewage, factory wastewater, hospital wastewater and aquaculture wastewater; and solid waste dumped on soil, and then leached into groundwater or washed into surface water via surface water runoff, comprising sludge from WWTPs, excretion from livestock and waste solid from landfill. We assumed the influent concentration of PPCPs in WWTPs as the concentration in urban raw untreated wastewater [30,31]. In the investigation, we adopted the PPCPs concentration in influent and effluent, excess sludge, hospital wastewater and livestock

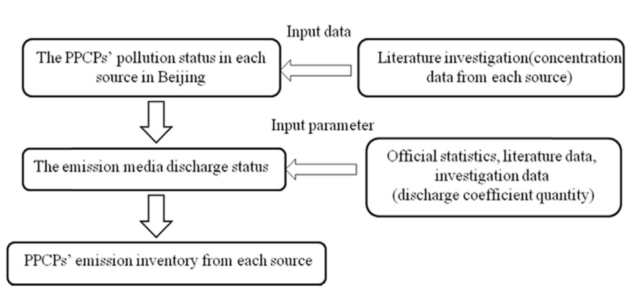

Fig. 1. Investigation method of discharge loads of PPCPs in Beijing.

wastewater as the local pollution data in Beijing, while concentration in aquaculture wastewater, landfill leachate and livestock excretion was estimated by the average concentration data at national level due to lack of local data. Meanwhile, we summed up the sample numbers of inflow and outflow and PPCPs concentration in hospital wastewater in the supporting information. Here, the PPCPs discharge from drug industries was not included due to the poor related data reported. The PPCPs pollution load in untreated wastewater was obtained via concentration of PPCPs in inflow to WWTPs. The volume of wastewater was acquired from the Beijing Statistical Yearbook[31]. In the estimate process, if the concentration data was given in scope in literature, we calculated the statistics with the mean in the estimation, we calculated using ' 1/2 LOQ (limit of quantitation)', or ' 1/2 LOD (limit of detection)' if the concentration was 'ND'. The statistics was listed in Tables S1,S3,S4. The calculation method was shown in Table S2.

On the whole, we have searched articles involving 119 PPCPs substances. The dominant group was antibiotics, followed by psychiatric drugs, anti-inflammatory drugs and personal care products. Some official statistics was calculated from China Statistics Yearbook 2013 [32], China Animal Husbandry Yearbook 2013 [33], The Chinese Fishery Yearbook 2013 [34], Chinese Medicine Statistical Yearbook 2011 [7] etc. Other statistics were sought through literature retrieval tools including Web of Science, Elsevier, Springer and Google, China National Knowledge Infrastructure (CNKI) and Wan Fang DATA etc.

Gap of discharge data related to all the pollution media was the main source of the uncertainty of the research. Besides, the detection method for different substances in different media as well as the difference of statistics method provided in the internet or reports also lead to the uncertainty. In the data processing, we had try our best to obtain a comprehensive information and reduce the miss distance between the statistics status and the actual status.

3. Results and discussion

3.1. The sources of PPCPs

The statistics results are involving 119 PPCPs pertaining to 11 categories (Table S1) in various pollution sources. The reported data related to hospital wastewater mainly focused on psychiatric drugs. Its emission quantity was classified into municipal wastewater, along with factory sewage [35]. For livestock and aquaculture farms, the statistics were mainly antibiotics [5,36,37]. Statistics concerning WWTPs comprised all kind of PPCPs categories [38–41].

3.1.1. Municipal wastewater

Generally, municipal wastewater treatment facilities collected the water via municipal pipeline from residential area, hospitals and manufacturers, when public utilities were complete [17]. In WWTPs, the municipal wastewater was processed mainly in some methods such as activated sludge method connected with oxidation ditch, biological membrane technology. In Beijing, more than 70% of sewage was treated by activated sludge method [42]. Traditional sewage treatment process including activated sludge method, oxidation ditch (OD) and biological membrane (BMR) method showed high efficiency in removing macromolecular particles in sewage, such as inorganic particles and macromolecular organic matters [1,28,43]. However, removal efficiency of PPCPs was low due to their special physicochemical characteristics of PPCPs (molecular conformation, Kow (octanol-water partition coefficient)) and WWTPs' operation condition (BOD, HRT, SRT, pH and temperature etc.) [2,44]. Actually, adsorption and biodegradation are dominant processes in WWTPs where the molecules tend to transfer between different matrix and structures, but are difficult to be mineralized completely [9,45].

The PPCPs' discharge quantity from WWTPs was shown in Fig. 2. On the whole, seventy-three substances comprised of sixty-five drugs and eight personal care products were studied. Drugs mainly comprise antibiotics, anti-inflammatories pharmaceuticals, anti-hyperlipidemias pharmaceuticals, anti-hypertension pharmaceuticals and psychiatric pharmaceuticals etc. The antibiotic categories contain quinolones, sulfanilamides, macrolides and tetracyclines. For sulfathiazole, sulfamethoxazole and sulfanilamide had large discharge quantities (381.89 kg, 352.89 kg and 277.96 kg respectively), and sulfamethoxazole's consumption (1331.85tons) was the highest in sulfonamide category during 2011 [7]. As a new generation macrolide antibiotic, erythromycin was frequently used in upper respiratory tract bacterial disease treatment and the discharge amount (196.05 kg) was the most. The high discharge quantity of erythromycin was mainly due to its large consumption and low Kd coefficient [46]. For tetracycline category, oxytetracycline had large quantity both in discharge (174.65 kg) and consumption (5193tons in 2011). Roman et al. found that most tetracycline molecules were excreted out of body after reacting with target organs, the excretion ratio was up to 90% [47]. It was reported that tetracycline tend to be wiped out soon after combined with cation and anion through their local electric charge under suitable pH [48,49]. For central nervous system drugs, sulpiride and carbamazepine had large emission quantity. Carbamazepine was efficient in epilepsy and schizophrenia treatment and was also frequently detected in environment [50]. A study on the fate of 22 central nervous system drugs in five WWTPs in Beijing showed that the fate of pharmaceuticals were closely related with the consumption pattern of the local residents [51].

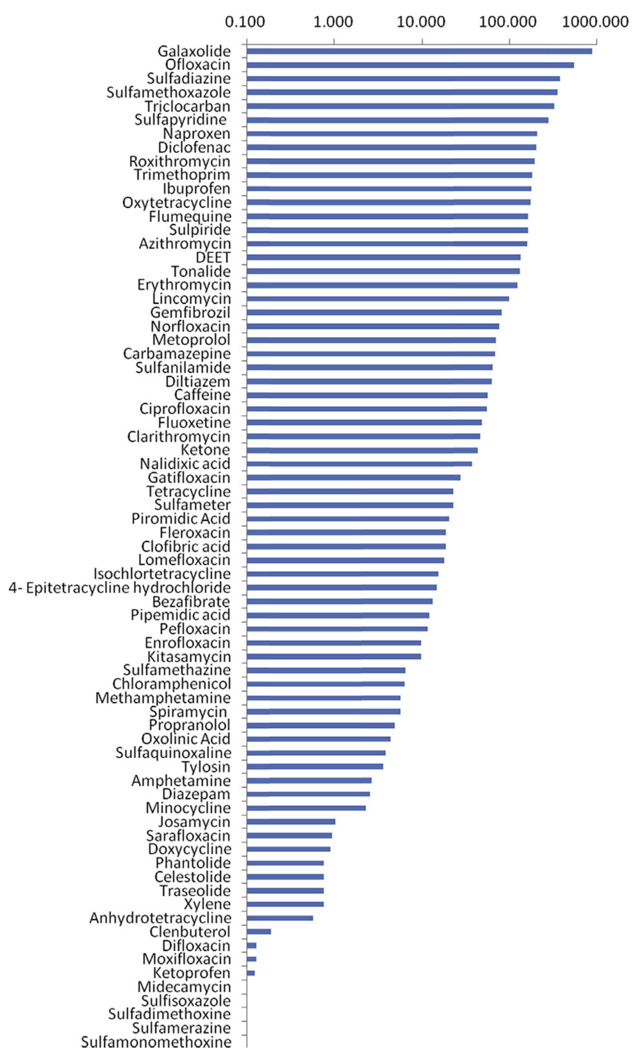

Fig. 2. Annual discharge loads of PPCPs from WWTPs in Beijing (unit: kg/yr).

It can be seen, the removal efficiency was varying among different PPCPs. Caffeine showed the highest removal rate (99%), while sulpiride (<50%) and carbamazepine (<10%) removal rates were rather low [38,52]. Sulfonamides' main removal process is biodegradation in activated sludge in treatment units and their Kd coefficient (32.6–352 L/kg) was low, leading to a low removal rate. However, quinolones have high removal efficiency and the dominant removal process was adsorption. It holds high Kd coefficient (642–8116L/kg) in WWTPs and was mainly absorbed and stored in sludge [53]. Quinolones were easily adsorbed to suspended particulates after urban wastewater entered WWTPs and their distribution ratios in sludge were higher than others (NOR, OFL and CIP was 91.6%, 84.4% and 90.8% respectively) [54]. The process of contaminant removal in different sewage types should be varied since the pollution contents are changing correspondingly. Besides, related wastewater treatment technology should be updated to deal with the new pollution patterns.

3.1.2. Untreated wastewater

The untreated wastewater significantly contributed to PPCPs pollution in Beijing, ranging from 53% (carbamazepine) to 99% (caffeine)(Fig. 3). Caffeine is used in drinks and psychoactive disease treatment and is easily biodegraded in wastewater (>85%) and other environmental matrices [50,52,55]. In the research, caffeine level in influent was nearly 50 times higher than that in effluent, the high removal efficiency in WWTPs and high concentration in aquatic environment indicated a large amount of raw untreated wastewater poured into the urban river. In contrast, carbamazepine from WWTPs contribution was owing to its degradation resistance. It was pointed out WWTPs just played a dilution role to the river from non-point sources in upstream in London [56]. Dai et al. had performed PPCPs source apportionment in a seriously polluted River (Beiyun river) in Beijing, using principal component analysis with multiple linear regression (PCA-MLR) method. The result showed that raw wastewater from discharge outlet contributed over 60% of PPCPs [17], suggesting some significant point or nonpoint sources may exist along the river [29,30,43].

3.1.3. Sludge

Along with the increasing of the quantity of municipal wastewater, the amount of concentrated sludge (moisture content 80%) in WWTPs has increased to 1.14 million tons in 2012 from 1.035 million tons in 2008 [52,57]. Correspondingly, the PPCPs' total emission quantity was nearly 1.59 tons in Beijing (Table S1). The collected data was mainly about antibiotics and perfume, such as HHCB (Galaxolide) and AHTN (1-(5,6,7,8-tetrahydro-3,5,5,6,8,8-hexamethyl-2-naphthyl)ethan-1-one), whose emissions were (2112.80 kg and 1322.40 kg) 1 or 2 orders of magnitude higher than others (Fig. 4). For antibiotics, quinolones' emission quantity was the maximum, among which ofloxacin (1170.75 kg) and norfloxacin (675.40 kg) were 1–2 orders of magnitude higher than others. Quinolones were the dominant antibiotic in excess sludge since their special adsorption properties were strong than other categories [58,59].

Presently, WWTPs in China have not been equipped effective facility to remove PPCPs thoroughly yet and quite a portation of the excess sludge was just piled up and poured away directly without

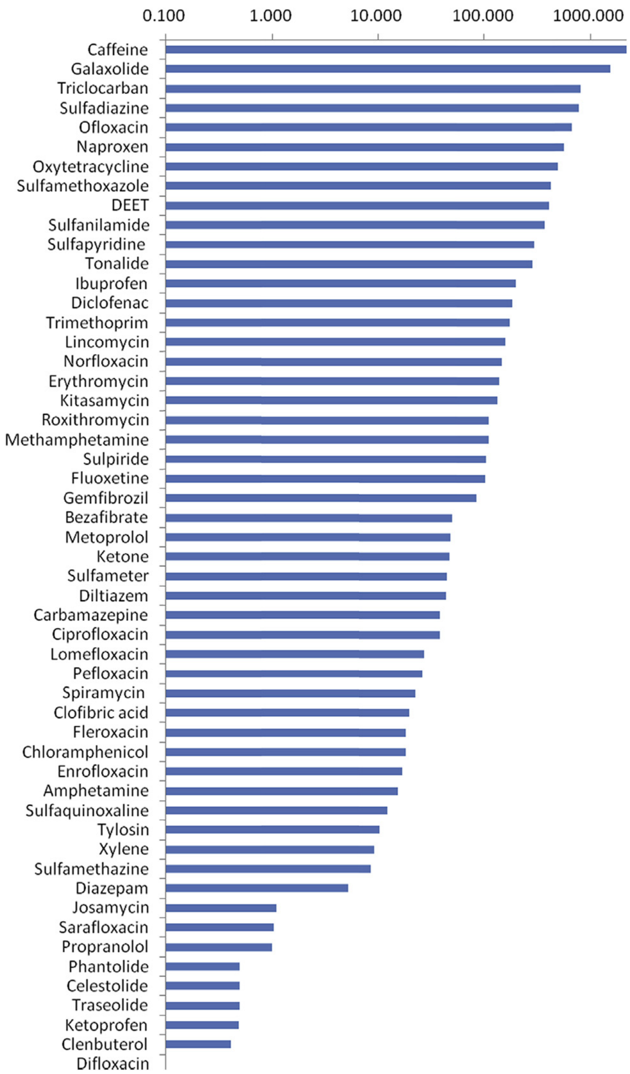

Fig. 3. Annual discharge loads of PPCPs in untreated wastewater (unit: kg/yr).

advanced treatment or packed and utilised as fertilizers into farmland nearby. However, the discharge amount of sewage and sludge has been increasing during the urban development. It was reported that 10 out of 15 planned sludge treatment facilities in WWTPs was laied aside in Beijing (http://epaper.jinghua.cn/html/2015-11/30/content_256932.htm). Annually, an emitted sludge quantity of 480,000 tons in Beijing accounted for 42% of the total amount, which would bring secondary pollution if inappropriately disposed [59].

3.1.4. *Hospital sewage*

In hospital wastewater, the PPCPs was lower and most substances were central nervous system drugs (Fig. 5). In result, sulpiride had the highest discharge quantity (82.83 kg), followed with clozapine (62.34 kg). Sulpiride was widely used in clinic or hospitals as it shows efficient property to treat diseases of hallucinations, delusions and insanity [2,15]. Pollution situation of pharmaceuticals in hospital effluent has close correlation with the population density, consumption pattern and local economy development [60].

Hospital wastewater was mainly released into WWTPs if the pipeline was constructed completely and the pollution substances would be removed along with the municipal wastewater. Hospital

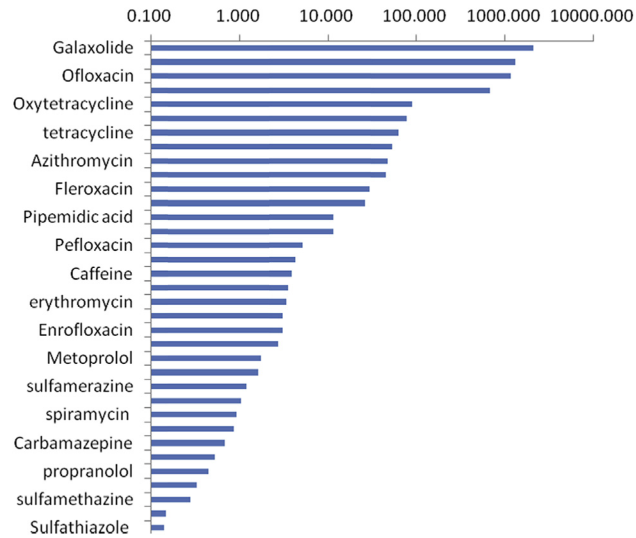

Fig. 4. Annual discharge loads of PPCPs in WWTPs' sludge in Beijing (unit: kg/yr).

has been considered as an important PPCPs pollution source to urban aquatic environment because in some cases it was likely to be poured to the urban river directly after mixed with the raw wastewater [29]. Moreover, it was pointed out that most psychiatric drug concentration in hospital sewage were higher than those in WWTPs' effluent [61]. Although the total emission load of PPCPs was less (Table S1), the annual injection with high pollution

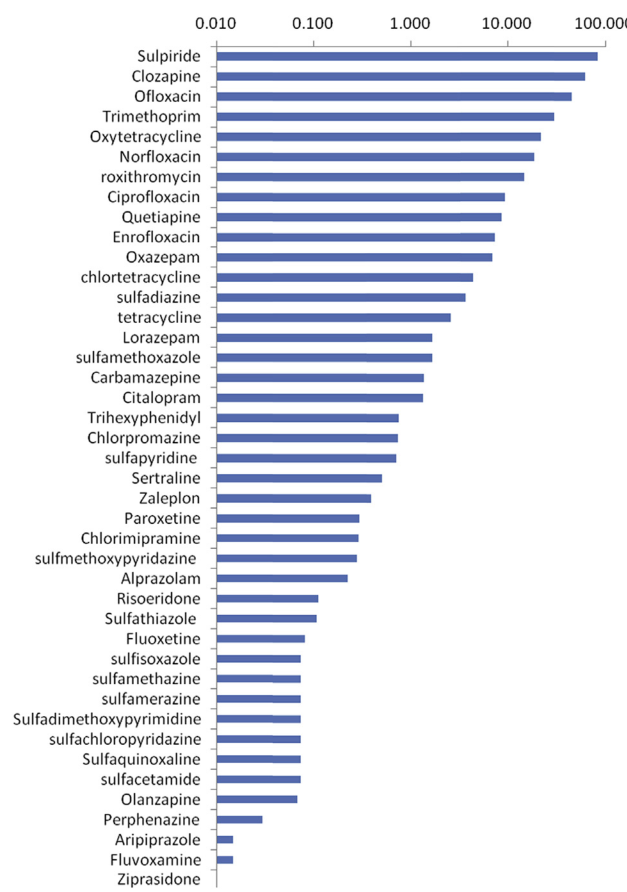

Fig. 5. Annual discharge loads of PPCPs in hospital wastewater in Beijing, China (unit: kg/yr).

concentration would also lead to a risk of drug resistance.

3.1.5. Aquaculture

The increase of production and consumption of aquiculture products in China promoted economic development in a certain extent [62]. It also brought a series of problems such as bacterial resistance and aquatic ecosystem deterioration [63,64]. In Beijing, the actual aquaculture area had increased to 8088.2 ha, among which the inland aquiculture area accounted for over 70% [65]. As a PPCPs pollution source [66], aquaculture area in Beijing had increased to 23 thousand hectares, it included industrial aquaculture farms, entertainment aquaculture farms, leisure fishing ponds, fishing places and fry fish hatcheries which need antibiotics in long-term to maintain its production status [34].

PPCPs substances were less reported in aquaculture, but their discharge quantities were great (Fig. 6). The PPCPs with discharge quantity over 100 kg were ciprofloxacin (925.35 kg), enrofloxacin (399.47 kg), oxytetracycline (244.59 kg), ofloxacin (181.61 kg) and sulfamethoxazole (166.50 kg), respectively. As a quinolone drug, ciprofloxacin has been abandoned by the Chinese Ministry of Agriculture, but its high concentration level (ug/L) was frequently detected in wastewater [67]. Quinolones show remarkable antibacterial ability owing to their wide antimicrobial spectrum property, but long-term usage in the prevention of bacterial diseases also tend to bring risk of bacterial resistance [16]. Normally, farmers always concern more with the increasing of aquatic product quantity, less on problems related to human health and ecological issues. Campbell et al. found that oxytetracycline could be detected after 70 days in sea-urchin's tissue and in the meantime the untoward reaction still affected their organism [68]. Bruun et al. had showed that the percentage of oxytetracycline resistant bacteria was over 50%, which decreased its target efficiency [69]. In short, the environmental PPCPs exposure to aquatic organism and human has become a new issue [1,2], attention should be paid on the transport and transform, as well as the bacterial resistance through scientific research.

3.1.6. Livestock

As showed in Fig. 7, the available PPCPs were all antibiotics, for livestock industry. The discharges of seven substances in two categories (tetracyclines and sulfonamides) were over 1 ton. In poultry and cattle farms, quinolones, tetracyclines and sulfonamides were dominant, while tetracyclines, sulfonamides and macrolides were the main contaminants in swine farms. Tetracyclines and sulfonamides were seriously polluted in livestock, it was frequently detected in environmental media and animal derived food [22,70,71]. Compared with other pollution, the situation in livestock was the most serious, suggesting a poor environmental management [16,72].

With the transformation of agriculture and the increase of human demand for animal products, the scale and production quantity of livestock had expanded rapidly. Livestock density and contaminant concentration in Beijing suburbs (Shunyi, Fangshan, Tongzhou, Daxing, Changping district) was much higher than those in eco-conserving districts (Pinggu, Huairou, Miyun, Yanqing, Mentougou district) [33,73–76] and same phanomenon also appeared in Shanghai where clear layers in different livestock density were distributed [77]. Besides, most livestock facilities were built without seriously considering the surround environment pollution. After application in livestock, most pharmaceuticals were excreted [3,78] and entered the environment. To reduce antibiotics pollution in livestock, the government had taken relevant measures in aspects including production, usage, business and export of veterinary pharmaceuticals [79]. But the pollution situation was still serious. It was reported that 40% large-scaled farms were constructed near the residential area in China and 70% swine farms eliminated excretion and feed residue through water-wash directly, few livestock farms installed facility to removal contaminants [16,80–82].

3.1.7. Landfill

Discharge quantities of PPCPs in landfill leachate were all under 10 kg (Fig. 8). Erythromycin had a great discharge amount which

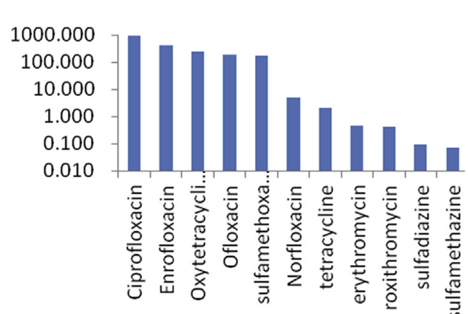

Fig. 6. Annual discharge loads of PPCPs in aquaculture wastewater (unit: kg/yr).

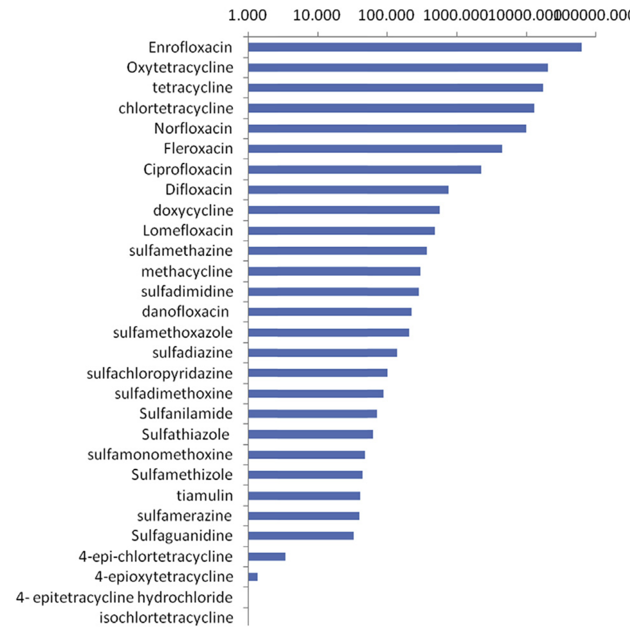

Fig. 7. Annual discharge loads of PPCPs in livestock in Beijing (unit: kg/yr).

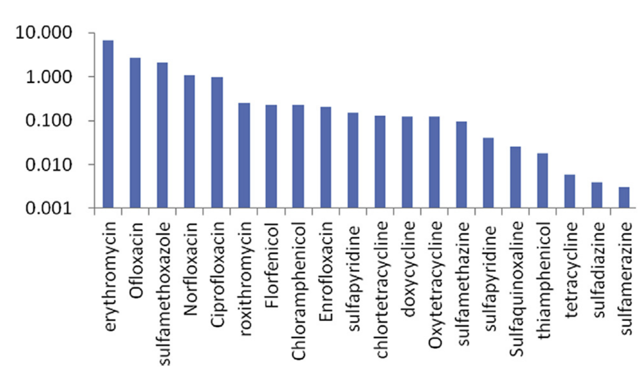

Fig. 8. Annual discharge loads of PPCPs in landfill leachate (unit: kg/yr).

was significantly related with its consumption (379.6 tons in 2011) [7]. Chloramphenicol was once frequently used in typhoid and paratyphoid treatment. It was prohibited at present due to its adverse effect in human hematopoietic system [83–85]. However, the presence of chloramphenicol still was observed in livestock excrement and aquaculture water, as well as the leachate in landfill [86]. After disposed, active substances in unused drugs from resident houses and hospitals are very likely concentrated in landfill leachate at high concentration level (1–3 magnitude orders higher than WWTPs effluent) [87].

3.2. The pollution and discharge of different PPCPs

3.2.1. The discharge quantity of different PPCPs

Fig. 9 shows the discharge quantities of PPCPs from all the pollution sources. The compounds with discharge quantities over 10 tons were all antibiotics. For quinolones, discharge quantity of norfloxacin was the highest mainly because most quinolones substance were massively used, they were frequently detected both as ingredients and metabolites [15,88,89]. Discharges of caffeine, HHCB, AHTN and triclocarban were between 1 and 10 tons. Among central nervous system drugs, sulpiride discharge was the largest. All in all, large emission quantity indicated that raw wastewater source and inefficiency of process in WWTPs [15,90]. Regulatory environmental risk assessment approaches should be taken into consideration about the pollutants discharged to surface waters from wastewater treatment systems, aquaculture facilities, and runoff from soil after manure application [2,91]. A comprehensive understanding of the discharge mechanisms and exposure pathways for PPCPs is therefore needed.

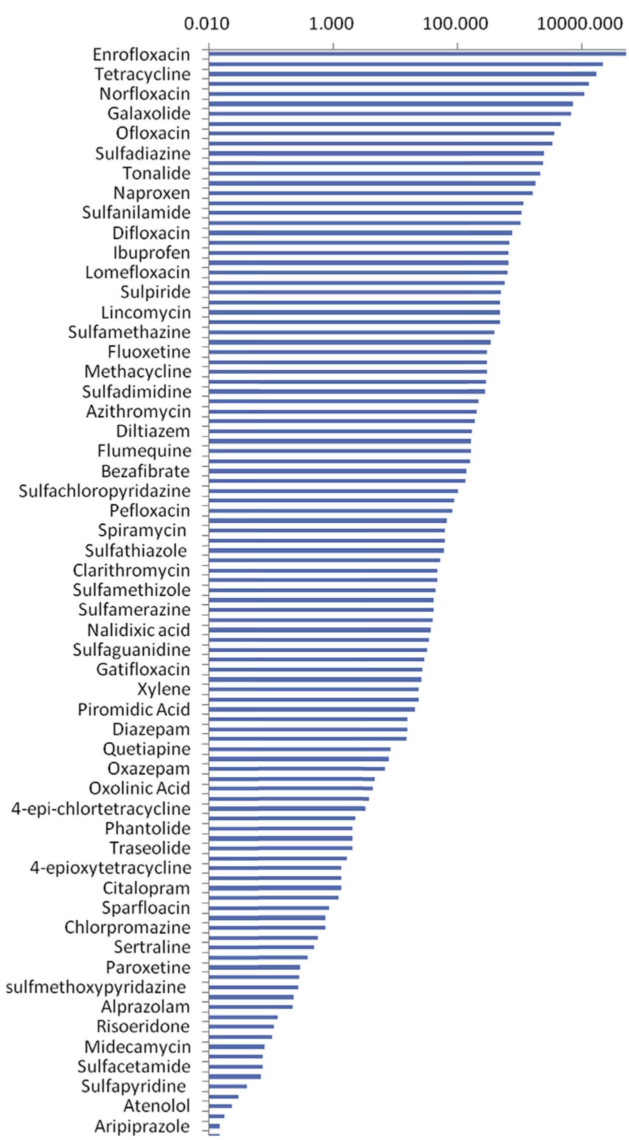

Fig. 9. Total discharge quantities of PPCPs in Beijing (unit: kg/yr).

3.2.2. The pollution and discharge in different media

Fig. 10 compared the concentrations of four frequently used antibiotics in liquid phase including urban sewage, aquaculture wastewater, leachate in landfill, hospital wastewater and urine and manure from swine livestock. Concentration detected in liquid excrement was 1–2 orders of magnitude higher than WWTPs influent and effluent. Concentration in swine livestock was the highest while the concentration in WWTPs effluent was the lowest. Four antibiotics, including ofloxacin, enrofloxacin, sulfamethoxazole and oxytetracyline, almost occurred in all the six sources. Sulfamethoxazole and oxytetracycline appeared in all the discharged liquid phase related to both human and animal used pharmaceuticals. Ofloxacin and enrofloxacin were seldom reported in excrement in livestock, but occurred in aquaculture wastewater in high concentration. In aquatic circulation, most discharged contaminants in multiple media eventually end up in surface water and was likely to occur in tap water. Risk assessment of antibiotics and their metabolites, especially veterinary antibiotics, as well as the exposure pathways, should be taken attention as it has been a critical challenge.

Fig. 11 compared the concentration of six pharmaceuticals in

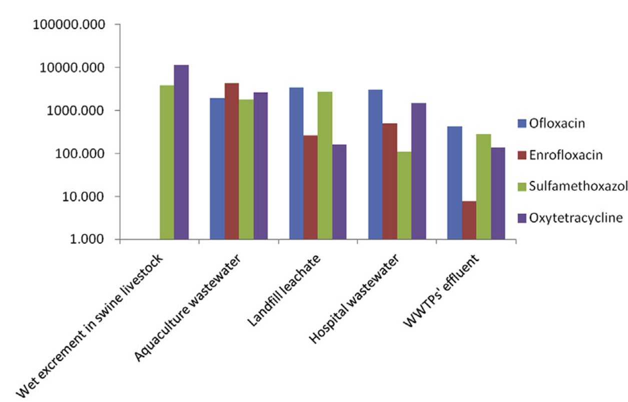

Fig. 10. Comparison of concentrations of PPCPs in liquid phase (unit: ng/L).

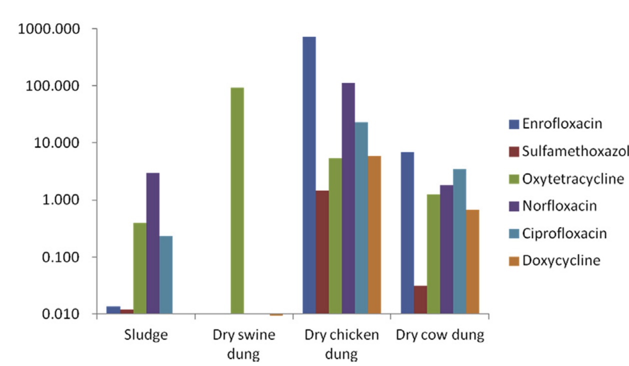

Fig. 11. Comparison of concentrations of PPCPs in solid phase (unit: mg/kg).

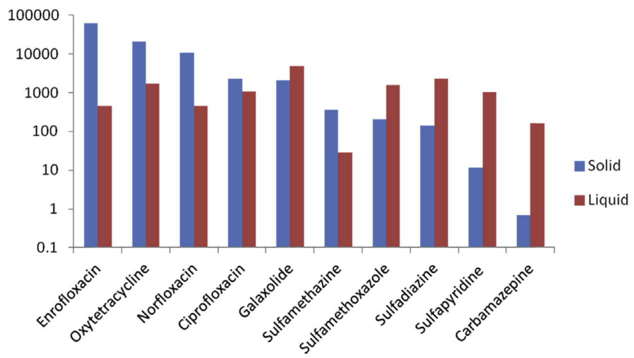

Fig. 12. Comparison of emission loads in soil and liquid (unit: kg/yr).

solid source media, including WWTP sludge and dry dung in swine, chicken and cow livestock. As can be seen, the concentration in chicken dung were quite higher than that in other pollution media. Oxytetracycline occurred in great concentration in all discharge media, its proportion in livestock was nearly 90%. Norfloxacin and ciprofloxacin has huge discharge quantity in sludge, chicken and cow dung. Actually, the six pharmaceuticals (enrofloxacin, sulfamethoxazole,oxytetracycline, norfloxacin,ciprofloxacin and doxycycline) were also frequently detected in other environmental sources including municipal wastewater, hospital wastewater and landfill leachate [29,92,93]. If consumed and applied together, many pharmaceuticals may cause adverse effect to organisms [94]. Long-term usage combined toxicity of chemical mixtures also should be taken into account for environmental risk assessment. Regulation related to pharmaceuticals in animal diseases treatment has been recently established in China, but the actual implementation is unsatisfactory. For example, people must get veterinary drug prescription when they want to buy drugs in particular cases [95],but unregulated usage and discharge of human and veterinary drugs frequently occurred [96,97].

Fig. 12 compared the discharge quantity of PPCPs into soil and water phases. Fate of all the pharmaceuticals was different along with the different substance characteristic. The substances shown in Fig. 12 were mainly antibiotics except for galaxolide and carbamazepine. The central nervous system drug carbamazepine occurred in higher quantity in liquid phase, while enrofloxacin mainly appeared in solid phase. Antibiotics, including enrofloxacin, norfloxacin and ciprofloxacin, might be prone to accumulate in solid, which should cause attention.

Aiming at the issue of the human and biological effect of antibiotics, especially the antimicrobial resistance, measures has been taken all over the world. The World Health Organization (WHO) has considered it as a threaten across the world (http://www.who.int/mediacentre/factsheets/antibiotic-resistance/zh/). The European Union had prohibited the usage of four antibiotics (monensin, salinomycin, avilamycin, flavomycin) in animal and human disease treatment in 2006. The Food and Agriculture Organization (FAO) of United Nations had forbad adding antibiotics into feed as supplement in livestock. In Japan, antibiotics must be undetected in animal-derived food when they are imported. Up to 2003, the consumption of antibiotics in China has reached up to 6000 tons [98,99], nearly half was used in animal disease prevention and treatment. Antimicrobial resistance had turned to a high risk, and it has brought a challenge to the production and usage of pharmaceuticals [100–102].

4. Conclusion

Based on the survey of various categories of PPCPs in multiple sources, we present a primary discharge inventory of environmental PPCPs loads in Beijing. Most of the investigated PPCPs were discharged in large quantity, mainly due to the huge usage amount and their difficulties in degradation. The discharge quantity in untreated wastewater was nearly 2 times higher than that in WWTPs. The distribution and removal efficiency in water and sludge in WWTPs were also different owing to their different molecule property. In general, the dominant removal mechanism in WWTPs were biodegradation and sorption. For personal care products, HHCB and AHTN had a great emission quantity in WWTPs. The PPCPs discharges from different sources had great relationship with the consumption patterns, especially antibiotics. Livestock farm was the most serious polluted source of antibiotics. In poultry and cattle farms, quinolones, tetracyclines and sulfonamides were the dominant, while tetracyclines, sulfonamides and macrolides were the main contaminants in swine farms. For waste solid leachate in urban landfill, abandoned drugs was frequently detected, and their contribution should not be neglected. Regulatory program for prospective environmental risk assessment of PPCPs should be taken into account combined with their toxicity in complex mixtures, especially for the antibiotics used in livestock. Scientific technologies should also be developed for the estimation of degradable PPCPs in food chains since some active compounds may pose a potential risk to related human and animal environment.

Acknowledgments

This work was financially supported by the National Natural Science Foundation of China (41503073), Tsinghua University Initiative Scientific Research Program, and Program for Changjiang Scholars and Innovative Research Team in University (IRT1261).

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.emcon.2016.07.001.

References

[1] K. Kummerer, Pharmaceuticals in the Environment: Sources, Fate, Effects and Risks, Springer Science & Business Media, 2008.
[2] A.B. Boxall, M.A. Rudd, B.W. Brooks, et al., Pharmaceuticals and personal care products in the environment: what are the big questions? Environ. Health Perspect. 120 (2012) 1221–1229.
[3] K. Kummerer, Drugs in the environment: emission of drugs, diagnostic aids and disinfectants into wastewater by hospitals in relation to other sources – a review, Chemosphere 45 (2001) 957–969.
[4] D. Ashton, M. Hilton, K. Thomas, Investigating the environmental transport of human pharmaceuticals to streams in the United Kingdom, Sci. Total Environ. 333 (2004) 167–184.
[5] J. Tolls, Sorption of veterinary pharmaceuticals in soils: a review, Environ. Sci. Technol. 35 (17) (2001) 3397–3406.
[6] C.G. Daughton, T.A. Ternes, Pharmaceuticals and personal care products in the environment: agents of subtle change? Environ. Health Perspect. 107 (1999) 907–938.
[7] CMIIT (China Ministry of Industry and Information Technology), Chinese Medical Statistical Yearbook 2011: Products Section, CMIIT, Beijing, China, 2012.
[8] M.A. Rudd, G.T. Ankley, A.B. Boxall, et al., International scientists' priorities for research on pharmaceutical and personal care products in the environment, Integr. Environ. Assess. Manag. 10 (2014) 576–587.
[9] J. Liu, M. Wong, Pharmaceuticals and personal care products (PPCPs): a review on environmental contamination in China, Environ. Internati 59 (2013) 208–224 (in Chinese).
[10] T. Heberer, Occurrence, fate, and removal of pharmaceutical residues in the aquatic environment: a review of recent research data, Toxicol. Lett. 131 (2002) 5–17.
[11] B.J. Richardson, P.K. Lam, M. Martin, Emerging chemicals of concern: pharmaceuticals and personal care products (PPCPs) in Asia, with particular reference to Southern China, Mar. Pollut. Bull. 50 (2005) 913–920.
[12] M. McBride, J. Wyckoff, Emerging liabilities from pharmaceuticals and

personal care products, Environ. Claims J. 14 (2002) 175–189.
[13] C.G. Daughton, Non-regulated water contaminants: emerging research, Environ. Impact Assess. Rev. 24 (2004) 711–732.
[14] H.P. Arp, Emerging decontaminants, Environ. Sci. Technol. 46 (2012) 4259–4260.
[15] Q. Bu, B. Wang, J. Huang, et al., Pharmaceuticals and personal care products in the aquatic environment in China: a review, J. Hazard. Mater. 262 (2013) 189–211.
[16] Q.Q. Zhang, G.G. Ying, C.G. Pan, et al., Comprehensive evaluation of antibiotics emission and fate in the river basins of China: source analysis, multimedia modeling, and linkage to bacterial resistance, Environ. Sci. Technol. 49 (2015) 6772–6782.
[17] B. Wang, G. Dai, S. Deng, et al., Linking the environmental loads to the fate of PPCPs in Beijing: considering both the treated and untreated wastewater sources, Environ. Pollut. 202 (2015) 153–159.
[18] L. Gao, Y. Shi, W. Li, et al., Occurrence of antibiotics in eight sewage treatment plants in Beijing, China, Chemosphere 86 (2012) 665–671.
[19] X. Zeng, G. Sheng, Y. Xiong, et al., Determination of polycyclic musks in sewage sludge from Guangdong, China using GC-EI-MS, Chemosphere 60 (2005) 817–823.
[20] J. Wang, x Zhang, Y. Guo, et al., Distribution and source analysis of synthetic musks in Shanghai sewage sludge, China Environ. Sci. 30 (6) (2010) 796–801.
[21] A.J. Ramirez, R.A. Brain, S. Usenko, et al., Occurrence of pharmaceuticals and personal care products in fish: results of a national pilot study in the United States, Environ. Toxicol. Chem. 28 (2009) 2587–2597.
[22] A.K. Sarmah, M.T. Meyer, A.B. Boxall, A global perspective on the use, sales, exposure pathways, occurrence, fate and effects of veterinary antibiotics (VAs) in the environment, Chemosphere 65 (2006) 725–759.
[23] Q. Sui, J. Huang, S. Deng, et al., Seasonal variation in the occurrence and removal of pharmaceuticals and personal care products in different biological wastewater treatment processes, Environ. Sci. Technol. 45 (2011) 3341–3348.
[24] X. Long, Urban and rural integration development research in Beijing, J. Central Inst. Social. 4 (2011) 92–96 (in Chinese).
[25] J. Li, A Preliminary Study on the Improvement of City Village in Beijing, Tsinghua University, Beijing, China, 2011.
[26] E.D. Sclar, P. Garau, G. Carolini, The 21st century health challenge of slums and cities, Lancet 365 (2005) 901–903.
[27] X. Hu, Y. Luo, Q. Zhou, Simultaneous analysis of selected typical antibiotics in manure by microwave-assisted extraction and LC-MS n, Chromatographia 71 (2010) 217–223.
[28] G.H. Dai, B. Wang, J. Huang, et al., Occurrence and source apportionment of pharmaceuticals and personal care products in the Beiyun River of Beijing, China, Chemosphere 119 (2015) 1033–1039.
[29] G.H. Dai, J. Huang, W. Chen, et al., Major pharmaceuticals and personal care products (PPCPs) in wastewater treatment plant and receiving water in Beijing, China, and associated ecological risks, Bull. Environ. Contam. Toxicol. 92 (2014) 655–661.
[30] G.H. Dai, B. Wang, J. Huang, et al., Occurrence and source apportionment of pharmaceuticals and personal care products in the Beiyun River of Beijing, China, Chemosphere 119 (2015) 1033–1039.
[31] Q.F. Xia, Beijing Statistical Yearbook, China Statistics Press, Beijing, China, 2013.
[32] L. Kong, Y. Song, China Statistics Yearbook, China Statistics Press, Beijing, China, 2013.
[33] L.S. Kong, China Animal Industry Yearbook, China agriculture press, Beijing, China, 2013.
[34] Z.S. Liu, S.M. Li, China Fisheries Yearbook, China agriculture press, Beijing, China, 2013.
[35] X. Zhang, T. Zhang, L. Dong, et al., Determination of antibiotics in hospital wastewater using HPLC-MS/MS coupled with solid phase extraction, J. Instrum. Anal. 31 (2012) 453–458.
[36] A. Ostermann, J. Gao, G. Welp, et al., Identification of soil contamination hotspots with veterinary antibiotics using heavy metal concentrations and leaching data—a field study in China, Environ. Monit. Assess. 186 (2014) 7693–7707.
[37] J. Li, B. Shao, J. Shen, et al., Occurrence of chloramphenicol-resistance genes as environmental pollutants from swine feedlots, Environ. Sci. Technol. 47 (2013) 2892–2897.
[38] H. Zhou, C. Wu, X. Huang, et al., Occurrence of selected pharmaceuticals and caffeine in sewage treatment plants and receiving rivers in Beijing, China, Water Environ. Res. 82 (2010) 2239–2248.
[39] H. Zhou, X. Huang, M. Gao, et al., Distribution and elimination of polycyclic musks in three sewage treatment plants of Beijing, China, J. Environ. Sci. 21 (2009) 561–567.
[40] U. Khan, A.L. van Nuijs, J. Li, et al., Application of a sewage-based approach to assess the use of ten illicit drugs in four Chinese megacities, Sci. Total Environ. 487 (2014) 710–721.
[41] J. Li, L. Hou, P. Du, et al., Estimation of amphetamine and methamphetamine uses in Beijing through sewage-based analysis, Sci. Total Environ. 490 (2014) 724–732.
[42] G. Zhang, Research and Plan on Peclaimed Wastewater Resue in Beijing, China agricultural university, Beijing, China, 2005.
[43] Y. Yang, J. Fu, H. Peng, et al., Occurrence and phase distribution of selected pharmaceuticals in the Yangtze Estuary and its coastal zone, J. Hazard Mater 190 (2011) 588–596.
[44] A. Garcia-Rodríguez, V. Matamoros, C. Fontzas, et al., The ability of biologically based wastewater treatment systems to remove emerging organic contaminants—a review, Environ. Sci. Pollut. Res. 21 (2014) 11708–11728.
[45] B. Li, T. Zhang, Biodegradation and adsorption of antibiotics in the activated sludge process, Environ. Sci. Technol. 44 (9) (2010) 3468–3473.
[46] A.L. Batt, S. Kim, D.S. Aga, Comparison of the occurrence of antibiotics in four full-scale wastewater treatment plants with varying designs and operations, Chemosphere 68 (2007) 428–435.
[47] R. Hirsch, T. Ternes, K. Haberer, et al., Occurrence of antibiotics in the aquatic environment, Sci. Total Environ. 225 (1999) 109–118.
[48] R.A. Figueroa, A. Leonard, A.A. MacKay, Modeling tetracycline antibiotic sorption to clays, Environ. Sci. Technol. 38 (2003) 476–483.
[49] A. Gulkowska, H.W. Leung, M.K. So, et al., Removal of antibiotics from wastewater by sewage treatment facilities in Hong Kong and Shenzhen, China, Water Res. 42 (2008) 395–403.
[50] Z.S. Lassi, A.M. Imam, S.V. Dean, et al., Preconception care: caffeine, smoking, alcohol, drugs and other environmental chemical/radiation exposure, Reprod. Health 11 (Suppl 3) (2014).
[51] S. Yuan, X. Jiang, X. Xia, et al., Detection, occurrence and fate of 22 psychiatric pharmaceuticals in psychiatric hospital and municipal wastewater treatment plants in Beijing, China, Chemosphere (2013) 2520–2525.
[52] Q. Sui, J. Huang, S. Deng, et al., Occurrence and removal of pharmaceuticals, caffeine and DEET in wastewater treatment plants of Beijing, China, Water Res. 44 (2010) 417–426.
[53] W. Li, Y. Shi, L. Gao, et al., Occurrence and removal of antibiotics in a municipal wastewater reclamation plant in Beijing, China, Chemosphere 92 (2013) 435–444.
[54] E.M. Golet, I. Xifra, H. Siegrist, et al., Environmental exposure assessment of fluoroquinolone antibacterial agents from sewage to soil, Environ. Sci. Technol. 37 (2003) 3243–3249.
[55] I.J. Buerge, T. Poiger, M.D. Muller, et al., Caffeine, an anthropogenic marker for wastewater contamination of surface waters, Environ. Sci. Technol. 37 (2003) 691–700.
[56] J.B. Ellis, Pharmaceutical and personal care products (PPCPs) in urban receiving waters, Environ. Pollut. 144 (2006) 184–189.
[57] W. Li, J. Wu, C. He, Monitoring and evaluation of the sludge characteristic in Beijing, Water Wastewater Inf. 4 (2014) 12–15 (in Chinese).
[58] Y. Zhang, X. Zhou, Environmental Pollution and Control of Pharmaceuticals and Personal Care Products, Beijing Science press, Beijing, China, 2012.
[59] X. Cui, W. Li, W. Xie, et al., Sludge treatment and disposal in municipal sewage treatment plant in Beijing, Water Wastewater Eng. 36 (2010) 17–20 (in Chinese).
[60] J.E. Hodges, C.M. Holmes, R. Vamshi, et al., Estimating chemical emissions from home and personal care products in China, Environ. Pollut. 165 (2012) 199–207.
[61] S. Yuan, X. Jiang, X. Xia, et al., Detection, occurrence and fate of 22 psychiatric pharmaceuticals in psychiatric hospital and municipal wastewater treatment plants in Beijing, China, Chemosphere 90 (2013) 2520–2525.
[62] R. Sanders, A market road to sustainable agriculture? ecological agriculture, green food and organic agriculture in China, Dev. Change 37 (2006) 201–226.
[63] D.J. Milan, T.A. Peterson, J.N. Ruskin, et al., Drugs that induce repolarization abnormalities cause bradycardia in zebrafish, Circulation 107 (2003) 1355–1358.
[64] A. Rico, Y. Geng, A. Focks, et al., Modeling environmental and human health risks of veterinary medicinal products applied in pond aquaculture, Environ. Toxicol. Chem. 32 (2013) 1196–1207.
[65] P. Gao, Y. Luo, Q. Zhou, et al., Research advancement of antibiotics resistance genes (ARGs) in aquaculture environment, Asian J. Ecotoxicol. 4 (2009) 770–779.
[66] D. Wang, Q. Sui, W. Zhao, et al., Pharmaceutical and personal care products in the surface water of China: a review, Chin. Sci. Bull. 59 (2014) 743–751.
[67] Y. Ruan, J. Chen, C. Guo, et al., Distribution characteristics of typical antibiotics in surface water and sediments from freshwater aquaculture water in Tianjin suburban areas, China, J. Agro-Environ. Sci. 30 (2011) 2586–2593.
[68] D.A. Campbell, Impact and residence time of oxytetracycline in the sea urchin, Psammechinus miliaris, a potential aquaculture species, Aquaculture 202 (2001) 73–87.
[69] A.S. Schmidt, M.S. Bruun, I. Dalsgaard, et al., Incidence, distribution, and spread of tetracycline resistance determinants and integron-associated antibiotic resistance genes among motile aeromonads from a fish farming environment, Appl. Environ. Micro. Biol. 67 (2001) 5675–5682.
[70] L. Wollenberger, B. Halling-Surensen, K.O. Kusk, Acute and chronic toxicity of veterinary antibiotics to Daphnia magna, Chemosphere 40 (2000) 723–730.
[71] Z. Yuan, Simultaneous Determination of 16 Sulfonamide Residues in Animal Food Products, Chongqing Medical University, Chongqing, Beijing, 2013.
[72] S. Ortiz de Garcia, G. Pinto Pinto, P. Garcia Encina, et al., Consumption and occurrence of pharmaceutical and personal care products in the aquatic environment in Spain, Sci. Total. Environ. 444 (2013) 451–465.
[73] H. Ma, A.N. Rae, J. Huang, et al., Enhancing productivity on suburban dairy farms in China, Agric. Econ. 37 (2007) 29–42.
[74] J. Wolf, M. Van Wijk, X. Cheng, et al., Urban and peri-urban agricultural production in Beijing municipality and its impact on water quality, Environ.

Urban 15 (2003) 141–156.
[75] L. Yang, Study on Treatment Technology and Processing of the Dispersed Swine Wastewater, Xi'an University of Architecture and Technology, Xi'an, Beijing, 2011.
[76] W. Li, Y. Li, M. Yang, et al., Spatial distribution of livestock and poultry production and land application accessibility of animal manure in Beijing, J. Nat. Resour. 25 (2010) 746–755.
[77] S. Wang, M. Chen, L. Yu, et al., Research of livestock and poultry pollution in Shanghai based on GIS, Agro-Environ. Prot. 20 (2001) 214–220 (in Chinese).
[78] B. Halling-Sorensen, Occurrence, fate and effects of pharmaceutical substances in the environment – a review, Chemosphere 36 (1998) 357–393.
[79] GOSC (General Office of the State Council of the People's Republic of China), Animal Medicine Management Regulations, GOSC, Beijing, China, 2004.
[80] GOSC (General Office of the State Council of the People's Republic of China), The Twelfth Five-year" National Urban Sewage Treatment and Recycling Facility Constructions Plan, GOSC, Beijing, China, 2012.
[81] E. Zuccato, S. Castiglioni, R. Fanelli, Identification of the pharmaceuticals for human use contaminating the Italian aquatic environment, J. Hazard. Mater. 122 (2005) 205–209.
[82] H. Chen, Y. Dong, H. Wang, et al., Residual characteristics of sulfanilamide in animal feces in Jiangsu province, J. Agro-Environ. Sci. 27 (2008) 385–389.
[83] A.K. Sarmah, M.T. Meyer, A.B. Boxall, A global perspective on the use, sales, exposure pathways, occurrence, fate and effects of veterinary antibiotics (VAs) in the environment, Chemosphere 65 (2006) 725–759.
[84] C.R. Suarez, E. Phillip Ow, Chloramphenicoi toxicity associated with severe cardiac dysfunction, Pediatr. Cardiol. 13 (1992) 48–51.
[85] A. Schmitt-Gräf, Chloramphenicol-induced aplastic anemia terminating with acute nonlymphocytic leukemia, Acta Haematol. 66 (4) (1981) 267–268.
[86] I. Robinson, G. Junqua, R. Van Coillie, et al., Trends in the detection of pharmaceutical products, and their impact and mitigation in water and wastewater in North America, Anal. Bioanal. Chem. 387 (2007) 1143–1151.
[87] L.Y. Sheng, China statistical Yearbook, China statistics press, Beijing, China, 2014.
[88] D.M. Whitacre, F.A. Gunther, Reviews of Environmental Contamination and Toxicology, Springer, 2012.
[89] S. Pérez, D. Barceló, Applications of LC-MS to quantitation and evaluation of the environmental fate of chiral drugs and their metabolites, TrAC Trends Anal. Chem. 27 (2008) 836–846.
[90] S. Kaplan, Review: pharmacological pollution in water, Crit. Rev. Environ. Sci. Technol. 43 (2013) 1074–1116.
[91] A. Calderbank, The Occurrence and Significance of Bound Pesticide Residues in Soil, Reviews of Environmental Contamination and Toxicology, Springer, 1989, pp. 71–103.
[92] X. Liang, Z. Shi, X. Huang, Occurrence of antibiotics in typical aquaculture of the Pearl river Estuary, Ecolo. Environ. Sci. 22 (2013) 304–310.
[93] W. Li, Y. Shi, L. Gao, et al., Occurrence and removal of antibiotics in a municipal wastewater reclamation plant in Beijing, China, Chemosphere 92 (2013) 435–444.
[94] E. He, E. Liu, Q. Zhang, et al., Sources and countermeasures of drug residues in animal-derived products, Animal Husb. Vet. Med. 5 (2012) 1–3 (in Chinese).
[95] CMA (China Ministry of Agriculture), Regulation for Veterinary Prescription and Non-prescription Drugs, Beijing, China, 2013.
[96] J. Li, L. Hou, P. Du, et al., Estimation of amphetamine and methamphetamine uses in Beijing through sewage-based analysis, Sci. Total Environ. 490 (2014) 724–732.
[97] B. Shao, D. Chen, J. Zhang, et al., Determination of 76 pharmaceutical drugs by liquid chromatography–tandem mass spectrometry in slaughterhouse wastewater, J. Chromatogr. A 1216 (2009) 8312–8318.
[98] S. Jin, Regulation, Realities and Recommendation on Antimicrobial Use in Food Animal Production in China, the MEdical Impact of the Use of Antimicrobials in Food Animals, WHO, Geneva, 1997 (Section 2.3. 4).
[99] M.A. Cole, R.J.R. Elliott, K. Shimamoto, Industrial characteristics, environmental regulations and air pollution: an analysis of the UK manufacturing sector, J. Environ. Econo. Manag. 50 (2005) 121–143.
[100] L. Cao, W. Li, Y. Chen, et al., The standardized use of the antibiotic feed additine in animal ausbardry production, Acta Ecol. Anim. Domastici 30 (2009) 105–110.
[101] F.C. Tenover, Mechanisms of antimicrobial resistance in bacteria, Am. J. Med. 119 (2006) S3–S10.
[102] M.L. Cohen, Epidemiology of drug resistance: implications for a post—antimicrobial era, Science 257 (5073) (1992) 1050–1055.