

Investigation on the fate of quinolone antibiotics in three drinking water treatment plants of China

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ABSTRACT

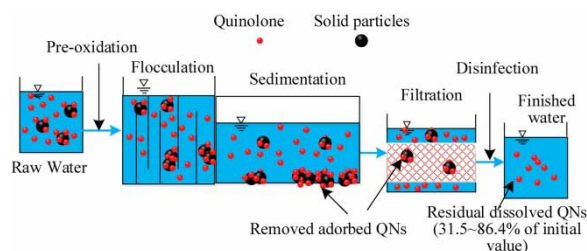
Quinolone (QN) antibiotics are widely used all over the world and have been frequently detected in source water, but the occurrence in tap water and the treatment efficiencies of QNs by drinking-water treatment plants (DWTPs) were rarely reported. In the present study, the occurrence and distribution of six representative QNs in three urban DWTPs of China were investigated. The results showed that the concentrations of total QNs in the three source waters ranged from 26.4 ng/L to 313.8 ng/L and all of the six QNs were detectable with a detection frequency of 100% (4.6 to 121.7 ng/L). Enrofloxacin (ENR) and ofloxacin (OFL) were the dominant species of QNs and accounted for 40.1% to 79.5% of the total QNs. After the treatments, there were still considerable QNs in the finished water (total amounts of 74.9 ng/L to 148.4 ng/L). The adsorbed QNs could be readily treated with the removal of turbidity by DWTPs, but only a part of the dissolved QNs (13.6% to 68.5%) can be removed. This implies that the dissolved QNs were more hazardous in the source water. Pre-oxidation and disinfection could remove $15.8 \pm 8.3\%$ and $16.9 \pm 10.8\%$ of dissolved QNs, respectively, depending on the chemical structure of QNs and the types of oxidant. Chemical oxidation was more efficient than coagulation-sedimentation and filtration for the treatment of dissolved QNs. Ozone-granular activated carbon filtration may fail to remove dissolved QNs in the actual DWTPs, because of the insufficient dosage of oxidant and the competition effect of natural organic matter.

Key words: antibiotics, drinking-water treatment, occurrence state, oxidation, quinolones (QNs)

HIGHLIGHTS

- Investigate the actual treatment efficiencies of QNs in three drinking water treatment plants of China.
- Compare the treatment efficiencies of dissolved and adsorbed QNs by typical water treatment progresses.
- Dissolved QNs are the bottleneck for the management of drinking water security.
- Chemical structure is the essential characteristic for efficient treatment of QNs by oxidation.

GRAPHICAL ABSTRACT



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ABBREVIATIONS

QNs	Quinolones
DWTPs	drinking water treatment plants
PPCPs	pharmaceutical and personal care products
EDCs	endocrine-disrupting chemicals
PIP	Pipemidic acid
NOR	norfloxacin
CIP	ciprofloxacin
ENR	enrofloxacin
OFL	ofloxacin
SAR	sarafloxacin
LOM	lomefloxacin
DW-A	drinking water treatment plant A
DW-B	drinking water treatment plant B
DW-C	drinking water treatment plant C
PACl	polyaluminum chloride
NOM	natural organic matter

1. INTRODUCTION

Quinolones (QNs) are the most-used antibiotics worldwide. They are broad-spectrum antibiotics and play an important role in the treatment of serious bacterial infections. Although QNs are well tolerated with mild to moderate side effects, the indiscriminate abuse of QNs may cause the spread of multidrug-resistant strains of bacteria. The adverse effects include toxicity to the central nervous system, convulsions, and hypoglycemia (Lee *et al.* 2014). Thus, it is recommended to minimize the use of QNs in less severe infections unless other antibiotic classes have been tried and failed (MacDougall *et al.* 2005).

However, the unexpected uptake of QNs may occur during daily water consumption. The production, transportation and application of QNs inevitably lead to the release of QNs into the aquatic environment. It is reported that many water sources of China (Figure 1) and other countries (Boleda *et al.* 2014) have been contaminated by QNs. If the water is not properly treated, the residual QNs may enter human bodies and cause certain health problems. Because drinking water treatment plants (DWTPs) are the last barrier for the security management of urban water supply, a survey about the occurrence and fate of QNs in DWTP can help researchers and DWTP managers to evaluate and reduce the unexpected exposure of QNs through drinking water supply systems.

Previous studies in recent years have monitored the occurrence of pharmaceutical and personal care products (PPCPs) and endocrine-disrupting chemicals (EDCs) including one or two representative QNs in water and wastewater treatment systems (Vieno *et al.* 2007; Pojana *et al.* 2011; Padhye *et al.* 2014). The residual QNs in the surface water environment were also investigated (Figure 1) (Jia *et al.* 2012; Wei *et al.* 2012; Dorival-Garcia *et al.* 2013). Compared with the investigation of wastewater treatment systems, the fate of QNs in DWTPs is rarely reported (Padhye *et al.* 2014; Cai *et al.* 2015; Yang *et al.* 2017). According to the limited literature available (Westerhoff *et al.* 2005), conventional water treatment processes are relatively ineffective in the removal of QNs, while advanced treatment technologies such as activated carbon, membranes and advanced oxidation may be feasible for the removal of the trace QNs. However, most of these studies consisted of laboratory experiments and full-scale investigations were scarce. Furthermore, the impacts of water quality and the existence forms of QNs (e.g., dissolved QNs and adsorbed QNs) on the performance of treatment processes are rarely studied. Therefore, the data presented may not reflect the actual situation. A full-scale investigation of the occurrence and fate of QNs in a DWTP is necessary and important.

In this study, the occurrence and fate of six selected QNs were measured in three representative urban DWTPs, which were distributed from northeastern to southern China with typical treatment processes adopted in China. The concentrations of QNs in different treatment units were measured and the removal efficiencies of QNs were calculated. The impacts of water quality and existence form of QNs on the removal of QNs were also evaluated. The objective of this study was to obtain a comprehensive understanding of the variation of QNs in source water and drinking water treatment systems. The results may be helpful for water treatment researchers and engineers to reveal the potential intake risk of QNs during daily water consumption and to improve the treatment efficiencies for QNs.

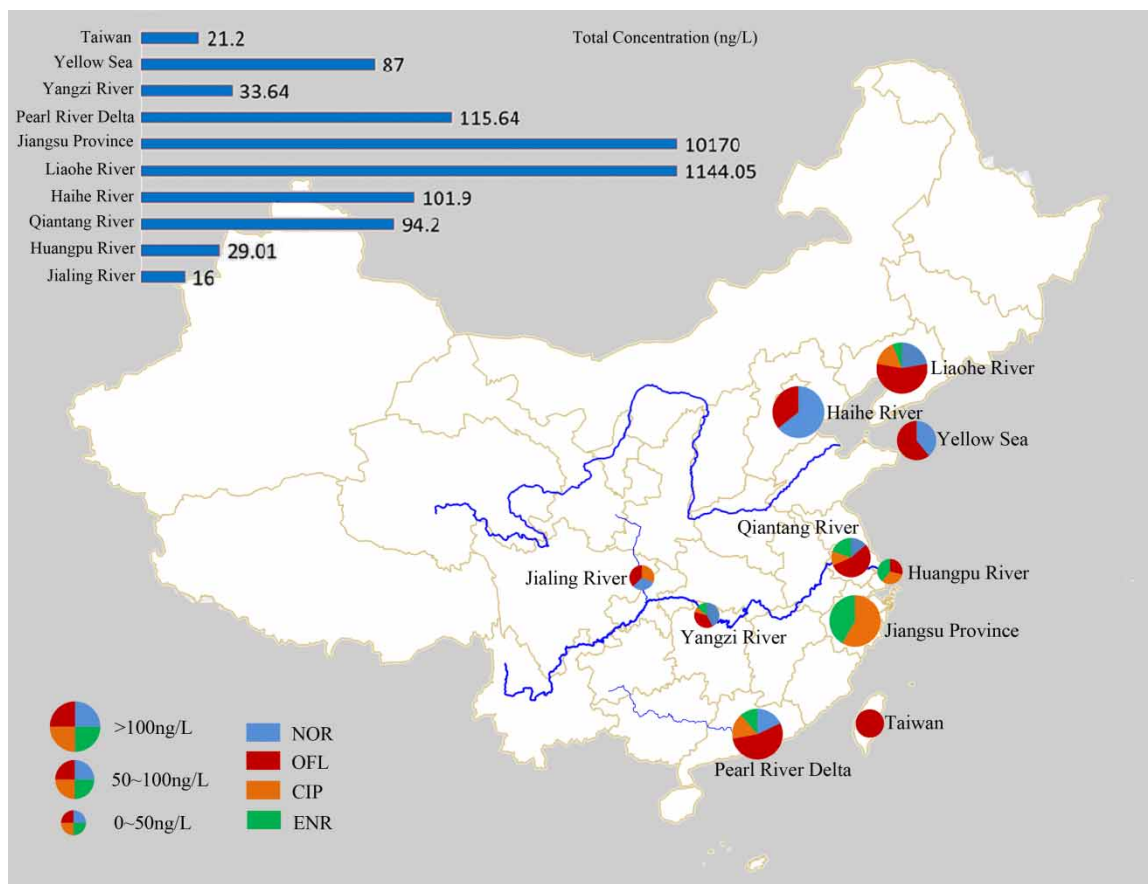


Figure 1 | QNs in the surface water of China according to studies in recent years (Chang *et al.* 2010; Jiang *et al.* 2011; Luo *et al.* 2011; Tong *et al.* 2011; Gao *et al.* 2012; Wei *et al.* 2012; Xu *et al.* 2013; Yan *et al.* 2013; Zhang *et al.* 2013; Bai *et al.* 2014; Lee *et al.* 2014).

2. MATERIALS AND METHODS

2.1. Chemicals and reagents

Pipemidic acid (PIP, 99.8%), norfloxacin (NOR, 98.5%), ciprofloxacin (CIP, 99.8%), enrofloxacin (ENR, 99.8%), ofloxacin (OFL, 99.5%), sarafloxacin (SAR, 99.8%) and lomefloxacin (LOM, 98.5%, used as an internal standard) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Methanol (HPLC grade) were provided by TEDIA (Charlotte, NC, USA). Phosphoric acid was purchased from Bodi Chemical Limited Company (Tianjin, China). Ethylenediamine tetraacetic acid disodium salt solution (Na₂EDTA) was obtained from Panreac AppliChem (Heidelberg, Germany). Formic acid (HPLC grade) was supplied by Merck (Darmstadt, Germany). Water for chromatographic purposes was purified using a Milli-Q system (Merck Millipore, Darmstadt, Germany).

Individual stock solutions were prepared in purified water/methanol solution (50/50, v/v) at a concentration of 500 mg/L and were used within one month. The working standard solutions were prepared weekly by diluting the analytical standards with purified water/methanol (50/50, v/v) to avoid solvent evaporation during the sample storage period. Both the standard solutions and sample extracts were stored in brown glass vials at 4 °C in the dark.

The solid-phase extraction (SPE) column (Oasis HLB 500 mg, 6 mL) was purchased from Waters Corporation (Milford, MA, U.S.A). Filters, including glass fiber filter (0.45 μm) and Teflon[®] filter (0.22 μm), were obtained from Alphatech Systems Ltd (Auckland, New Zealand).

2.2. DWTP introduction and sampling site description

Investigations were performed in three urban DWTPs in various parts of China (from the northeast to the south), labeled as DW-A, DW-B, and DW-C. The treatment processes of the three DWTPs and the location of the sampling sites are shown in

Figure 2. The samples from different sites of each DWTP were collected at the same time, and the sampling work was repeated twice with one-month interval. The characteristics of the raw water are shown in Table S1.

DW-A draws raw water from a reservoir in the northeast of China with a freshwater yield of $5 \times 10^5 \text{ m}^3/\text{d}$. Raw water is pumped from the reservoir to a junction well and then flows through a chlorine dioxide (ClO_2) pre-oxidation unit. The pre-oxidized water is piped to the regulating well in DW-A. After a rapid-mix step, the flow enters grid coagulation basins where polyaluminum chloride (PACl) is added as the coagulant. The supernatant is separated at the inclined-tube sedimentation basins, and then the clarified water is filtered through sand filters. Finally, the filtered water is disinfected by ClO_2 at a dosage of 2 mg/L (Figure 2(a)).

Raw water of DW-B is taken from a reservoir on the Yellow River in northern China with a water inflow of $2 \times 10^5 \text{ m}^3/\text{d}$. The influent is pre-oxidized by potassium permanganate. After a two-stage rapid-mix, the flow enters into the Densadeg® clarifiers. Alum and polymers are used as the coagulants. The clarified water then flows to intermediate ozonation tanks equipped with three ozone contactors (ozone dosage of 0.5 mg/L). Afterward, the water enters up-flow granular activated carbon filters. The filtered water passes through sand filters, followed by a disinfection process with Cl_2 (Figure 2(b)).

DW-C is located in the south of China with a freshwater yield of $3 \times 10^5 \text{ m}^3/\text{d}$. The DWTP draws raw water from an upstream reach of the Beijiing River. DW-C uses a conventional treatment process similar to DW-A; that is, pre-chlorination, coagulation-sedimentation, sand filtration and chlorination (Figure 2(c)), and the treatment efficiency of QNs was similar to that of DW-A. Thus, only the raw water and the effluent were analyzed and discussed (the treatment performance of QNs in DW-C has been shown in Fig. S2, supporting information).

2.3. Conservation and preparation of QNs samples

The conservation and preparation methods were confirmed by pre-experiments and the operation procedure is shown in Figure 3. Water samples (4 L) were preserved with 1.6 g of Na_2EDTA and acidified to pH 2.5 with H_3PO_4 immediately after sampling according to the method of previous studies (Seifrtová *et al.* 2009; Gros *et al.* 2013). The samples were then stored in 4 L amber glass bottles with Teflon-lined caps and taken to the laboratory as soon as possible. All samples were stored in the dark at 4°C and analyzed within 3 days.

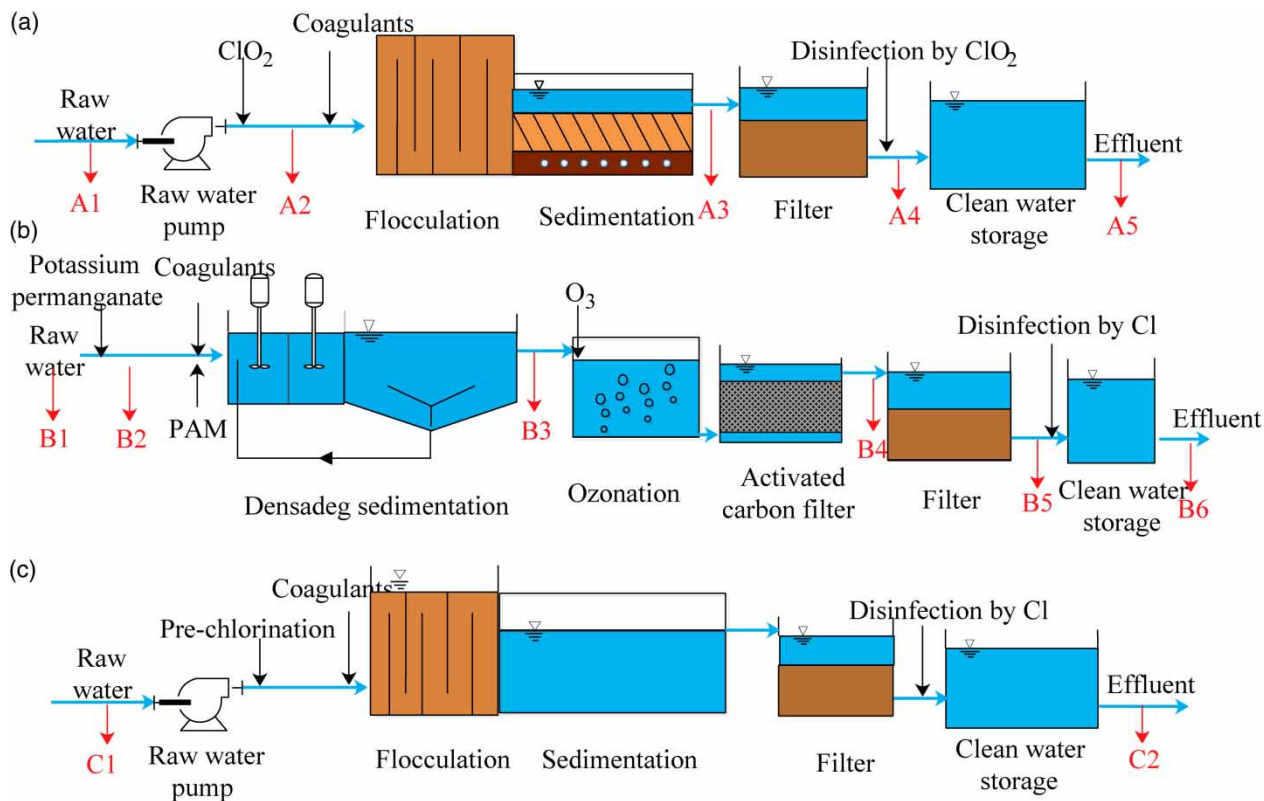


Figure 2 | Schematic of the treatment processes of the three DWTPs and locations of the sampling sites, (a) DW-A, (b) DW-B, (c) DW-C.

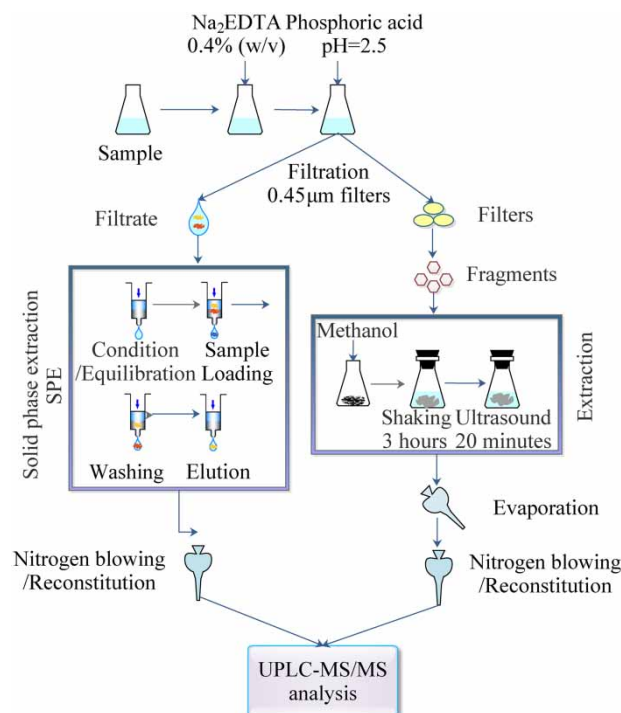


Figure 3 | Schematic of the pre-treatment method for dissolved and adsorbed QNs.

The water samples were filtered through 0.45 μm glass fiber filters. The filtrates (containing dissolved QNs) were extracted by a typical SPE procedure. Each 2 L sample was extracted at a sample loading rate of 2 mL/min through a 500 mg hydrophilic-lipophilic balance (HLB) cartridge pre-conditioned with 6 mL methanol followed by 6 mL Milli-Q water. After the sample loading process, the cartridges were rinsed with 6 mL Milli-Q water with 5% (v/v) of methanol at a flow rate of 2 mL/min. Then, the cartridge was dried for 20 min under vacuum and the analytes were eluted with 10 mL of 95% methanol/5% H_3PO_4 (pH 2.5) solution at a flow rate of 1 mL/min. The final extracts were evaporated to dryness at 30 $^\circ\text{C}$ under a gentle stream of nitrogen and then reconstituted in 1 mL of 20% methanol/80% H_3PO_4 solution (pH 2.5). The samples were transferred to amber HPLC vials and 0.5 mL of 100 $\mu\text{g/L}$ internal standards (LOM) were added. The recoveries of the six selected dissolved QNs were 72.1% to 117.58% in pure water, 71.3% to 100.67% in raw water and 64.68% to 119.17% in finished water.

The adsorbed QNs were extracted by methanol (approximate 5 mL per piece of filter). The filters with the intercepted solid particles containing adsorbed QNs were cut into pieces in the conical flask, and mixed with methanol. The conical flask sealed with Parafilm[®] was placed in an incubator shaker at 4 $^\circ\text{C}$ in the dark at a rotation rate of 100 rpm. After shaking for 3 h, the sample was put in an ultrasonic processor for 20 min. After filtration by Teflon[®] filters (0.22 μm pore size), the organic solvent was dried with anhydrous sodium sulfate and evaporated using a rotary evaporator in a K-D concentrator bottle. Finally, the samples were dried and reconstituted by the same procedure used for the dissolved QNs. The recovery of adsorbed QNs was not calculated because it was difficult for us to prepare an adsorbed QNs standard for the measurement of recovery. However, the extraction of adsorbed QNs was repeated after the first extraction and the QNs in the second extract were undetectable, which can indirectly prove the reliability of the extraction method.

2.4. QNs analysis

Prepared samples were analyzed by ultra-performance liquid chromatography-tandem mass spectrometry (UPLC-MS/MS) (Waters[®] XevoTM TQ MS Acquity UPLC System, Manchester, UK). The antibiotics were separated using an ACQUITY UPLC BEHTM C18 column (1.7 μm ; 2.1 mm \times 50 mm) (Waters, UK) at 30 $^\circ\text{C}$ with an injection volume of 25 μL . A binary gradient at a flow rate of 0.2 mL/min was used: mobile phase A was 0.2% (v/v) aqueous formic acid solution, and mobile phase B was 100% methanol. The gradient conditions were as follows: the gradient started with 80% A, then decreased to

30% (A) over a period of 5 min, and then to 0% within 0.1 min. This condition was held for 1.4 min to clean the column using mobile phase B. Finally, the mobile phase A was returned to 80% in 0.1 min and kept at that condition for 1.4 min to equilibrate the column. The total run time was 8 min.

Positive-mode electrospray ionization and multiple reactions monitoring (MRM) mode were used. The instrument parameters were as follows: capillary voltage, 3.0 kV; source temperature, 150 °C; desolvation temperature, 350 °C; desolvation gas flow, 650 L/h; cone gas flow, 50 L/h; collision gas flow, 0.15 mL/min. Nitrogen ($\geq 99.999\%$) was used as the cone and desolvation gas, and argon (99.999%) was used as the collision gas. Two sensitive MRM transitions were selected for each QN (the most intense one is used for quantification and the second one for confirmation). MassLynx software 4.1 was used to control the instrument and to obtain the data. The retention time and molecular ion of each QN, as well as the optimum cone voltages and collision energies are shown in Table S2.

The limits of quantitation of QNs in water were 1 ng/L except OFL (1.5 ng/L), according to 10 times signal-to-noise ratio. The details were shown in Table S3.

2.5. Analysis of other water quality indices

Other water quality indices, including temperature, pH, turbidity, color, ultraviolet absorbance at 254 nm (UV_{254}), total organic carbon, permanganate index and ammonia nitrogen (NH_3-N), were analyzed in the laboratories of the three DWTPs according to Chinese standard methods (Ministry of Health of the People's Republic of China & Standardization Administration of the People's Republic of China 2007), which are essentially consistent with the American Public Health Association standard methods (Water Environmental Federation & American Public Health Association 2005).

All of the measurements were taken in duplicate, and the arithmetic means were obtained and used as the final values.

3. RESULTS AND DISCUSSION

3.1. Occurrence of selected QNs in raw water

The QNs in the raw water of the three DWTPs were investigated twice between February and May, 2014, and the results are shown in Figure 4. The total concentration of QNs ranged from 26.4 ng/L to 313.8 ng/L. All of the selected QNs were detectable in raw water with a detection frequency of 100% (4.6 to 121.7 ng/L). OFL and ENR were the primary QNs in the raw water, which could account for 40.1% to 79.5% of the total QNs. These QNs could be present in raw water in either of two forms, i.e., the dissolved form (dissolved in liquid phase, red column in Figure 4) and the adsorbed form (adsorbed on the surface of suspended particles, blue column in Figure 4). Obviously, the QNs mainly existed in raw water as dissolved form, and the average proportions of dissolved QNs in DW-A, DW-B and DW-C were 87, 97 and 80%, respectively. Overall, the concentrations of QNs in the raw water decreased in the following sequence: DW-B > DW-A > DW-C.

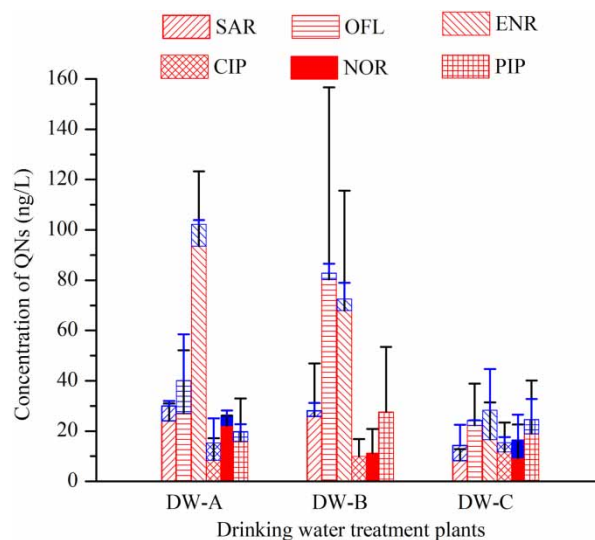


Figure 4 | Dissolved (lower red column) and adsorbed (upper blue column) QNs in the raw water of the three DWTPs.

The samples of raw water were collected from northeastern to southern China. Thus, the results implied that the QNs problem in source water was common in China. In fact, previous studies indicate many regions of China have been contaminated by different types of QNs with the total QN concentrations as high as 1,144.05 ng/L (Figure 1). Moreover, it is also reported that the same problems have also been found in Europe (Pojana *et al.* 2011; Boleda *et al.* 2014) and America (Padhye *et al.* 2014). Thus, the contamination of QNs has been a worldwide problem at present and should be an important issue for both environmental scientists and water treatment engineers.

It is interesting that the concentrations of QNs in the raw water of DW-B and DW-C varied much more significantly than that in DW-A (see the large error bars of DW-B and DW-C in Figure 4). The total QNs in the raw water of DW-A were 243.9 ng/L in the first survey and 190.4 ng/L in the second. However, the values in DW-B were 313.8 ng/L in the first survey and 149.9 ng/L in the second, and the values in DW-C were 26.4 ng/L and 250.7 ng/L, respectively. The variations of rainfalls may give a reasonable explanation. It was reported that spring run-off or storm flow could bring soil with off-flavor compounds into the surface water and cause odor incidents in lakes (Jensen *et al.* 1994; Zaitlin & Watson 2006). QNs may also be flushed into source water on rainy days. Take DW-C for example. There was only one rainfall event in April (before the first survey) but sixteen rainfall events between the two surveys, and the precipitation was approximate 480 mm in May 2014, almost 25% of the average annual precipitation in Guangzhou (Huang & Li 2014). The heavy storms brought soil into river and increased the turbidity of raw water from 5.26 NTU to 108 NTU. Thus, the adsorbed QNs on soil were also flushed into water, which caused the soar of QNs from 26.4 ng/L to 250.7 ng/L. The fact, the adsorbed QNs accounted for 40.11% of the total QNs in the second survey (compared with undetectable adsorbed QNs in the first survey), supported this explanation. This phenomenon indicates that QNs in raw water may mainly come from non-point source pollution.

3.2. Residual QNs in the finished water

The concentrations of QNs in the finished water of the three DWTPs are shown in Figure 5. Because the total concentration of QNs in the raw water of DW-C was very low (26.4 ng/L) on April 28th, QNs in the corresponding finished water were not analyzed on that day. After treatments, the adsorbed QNs were completely removed, but the removal ratios for dissolved QNs were only 13.6% to 68.5%. Thus, there were considerable residual QNs in the finished water of the three DWTPs. The total QNs (i.e., dissolved QNs) ranged from 74.9 ng/L to 148.4 ng/L. The six QNs were detectable in the finished water with the highest concentration of 70.4 ng/L. OFL and ENR were still the primary QNs in finished water, and the proportion even increased slightly to a range of 44.2% to 82.7%.

Although many previous studies indicate that there were QN problems in the aquatic environment, the QN problem in drinking water is rarely reported. Our finding indicated that QN problems did exist in drinking water. The concentration levels of specific QNs (from 1.7 ng/L to 70.4 ng/L) were in accordance with the previous study by Yiruhan *et al.* (2010). They measure the concentrations of NOR, CIP, and ENR in the tap water of Guangzhou and Macau and find the average

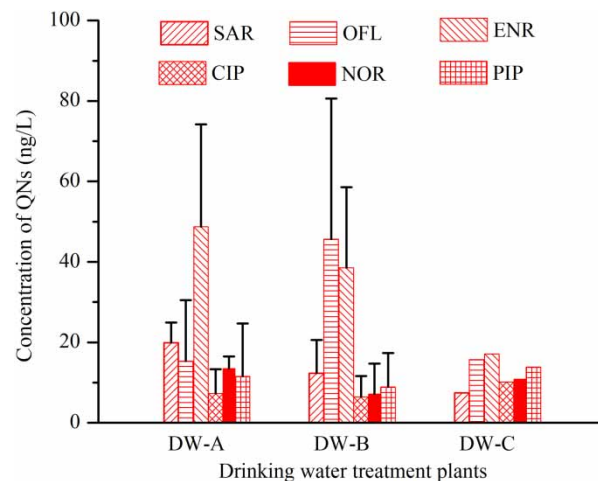


Figure 5 | Residual dissolved QNs in finished water of the three DWTPs. The adsorbed QNs were undetectable.

concentrations of NOR, CIP, and ENR are 9.0 ng/L, 4.0 ng/L, and 4.0 ng/L, respectively. Considering the health risk of QNs, it is important and necessary to investigate and improve the removal efficiency of QNs by drinking water treatment processes.

3.3. Fate of QNs during water treatment processes

3.3.1. Adsorbed QNs

DW-A and DW-C adopted conventional water treatment processes with pre-oxidation, while DW-B adopted advanced water treatment processes (pre-oxidation, coagulation-sedimentation, ozone-granular activated carbon and filtration). Therefore, the investigations were conducted in DW-A and DW-B to study the removal efficiencies of adsorbed QNs by different water treatment processes, and the results are shown in Figure 6. Because the concentrations of QNs were different in the raw water, all of the measured values were normalized (divided by the value in raw water) to minimize the interference of initial values. The error bars in Figure 6(a) represented the standard deviation between the two surveys. Because they only adsorbed SAR, OFL and ENR were detectable in the first survey for DW-B, the data in Figure 6(b) are shown without error bar.

Physico-chemical methods, including coagulation-sedimentation and filtration, are efficient for the removal of adsorbed QNs. The results indicated that more than 70% of the adsorbed QNs were removed by these processes and the residual amounts were lower than 10% of the initial adsorbed QNs in raw water after the filtration treatments (sand filtration for DW-A and granular active carbon filtration for DW-B). It is well known that coagulation-sedimentation and sand filtration can remove turbidity efficiently. The adsorbed QNs on suspended particles may also be well treated with the removal of turbidity, which can be supported by the analysis result of linear correlation between turbidity and residual adsorbed QNs ($r = 0.8414$) in DW-A and DW-B, as shown in Fig. S1.

In addition, the adsorbed QNs were undetectable after the treatment of disinfection. Considering the residual dissolved QNs in finished water (Figure 5), it is much more important for DWTPs to improve the treatment efficiency for dissolved QNs rather than that of adsorbed QNs.

3.3.2. Dissolved QNs

The variations of dissolved QNs along with the treatment processes of DW-A and DW-B are shown in Figure 7. Generally, oxidation treatment, including pre-oxidation and disinfection, could remove dissolved QNs more efficiently than physico-chemical treatment processes. The average removal rate of specific dissolved QNs by pre-oxidation and disinfection (removed QNs divided by the concentrations of QNs in the inflow of the unit) were $15.8 \pm 8.3\%$ and $16.9 \pm 10.8\%$, respectively, which were more than 2 times that by coagulation-sedimentation and filtration ($7.4 \pm 5.5\%$ and $3.0 \pm 5.1\%$).

The oxidation efficiency of QNs, including pre-oxidation and disinfection, could be affected by both the variety of QNs and oxidants. There were higher removal rates of OFL and ENR ($20.9 \pm 12.4\%$ for OFL and $24.8 \pm 7.4\%$ for ENR, on average) than those of other QNs ($5.8\% \sim 15.8\%$, on average) by disinfection (ClO_2 as the oxidant) in DW-A but lower removal rates ($6.1 \pm 0.8\%$ for OFL and $11.6 \pm 1.7\%$ for ENR, compared with $19.2\% \sim 36.8\%$ for others) by disinfection (Cl_2 as the oxidant) in DW-B. The different results could be attributed to the impacts of the chemical structure of these QNs. The piperazine ring of QNs is the primary reactive center toward oxidants. OFL and ENR are amines with a tertiary N4 functional group, while

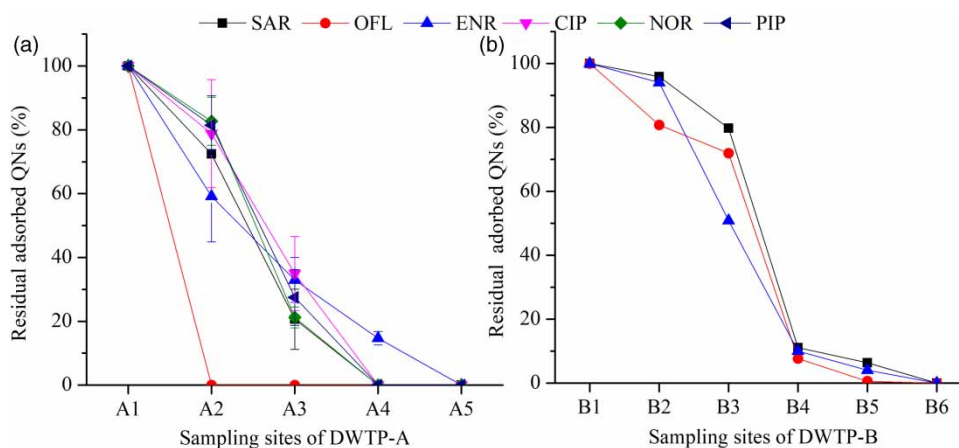


Figure 6 | Variations of adsorbed QNs along with the treatment processes of DW-A (a) and DW-B (b).

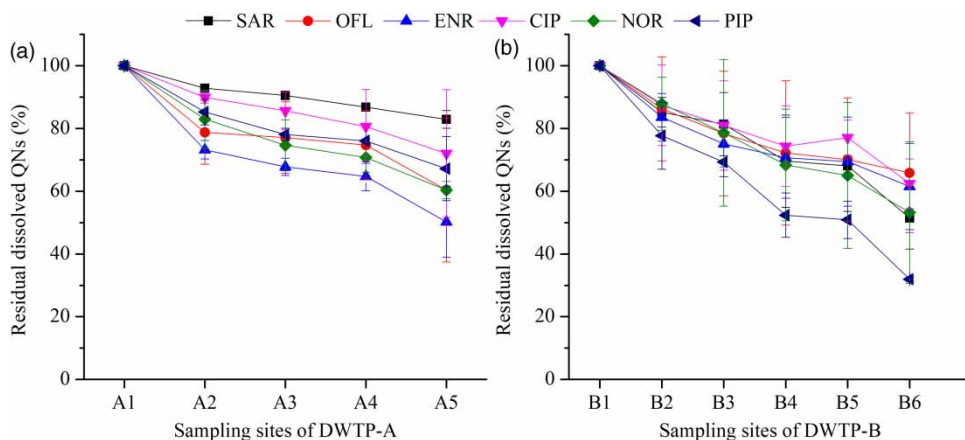


Figure 7 | Variations of dissolved QNs along with the treatment processes of DW-A (a) and DW-B (b).

the others are amines with a secondary N4 functional group. It has been reported that ClO_2 reacts with tertiary N4 functional groups much faster than secondary N4 functional groups (Wang *et al.* 2010). Thus, higher removal ratios of OFL and ENR were obtained in DW-A, which adopted ClO_2 as the oxidants (Figure 7(a)). In contrast, HOCl reacts with the tertiary amine more slowly than secondary N4 functional groups (Dodd *et al.* 2005). This is the reason that the removal rates of OFL and ENR dropped significantly in DW-B, which adopted chlorine as the disinfectants. In fact, similar phenomenon has been observed in DW-C, which also used traditional water treatment process (similar to DW-A) but adopted chlorine instead of ClO_2 as the oxidants. The removal rates of OFL and ENR (8.0% ~ 15.2%) by pre-chlorination and disinfection in DW-C were lower than other QNs (12.1% ~ 31.1%), and this fact supported the viewpoint that piperazine ring structures of QNs dominated the treatment efficiency by chlorine and ClO_2 .

Obviously, the species of oxidant can significantly affect the treatment efficiency of QNs. Because oxidation is the most efficient method for the removal of dissolved QNs in DWTPs, it is very important to choose an appropriate oxidant to improve the treatment efficiency, and the chemical structure of the dominant QNs should be seriously considered. According to the removal of QNs by disinfection in DW-A and DW-B and the fact that OFL and ENR were the dominant species of QNs in China (account for 40.1% ~ 79.5% of the total QNs in raw water), ClO_2 should be a better choice than chlorine for the management of QNs in DWTPs of China.

The removals of dissolved QNs by physico-chemical methods were negligible ($5.2 \pm 5.7\%$). Alexander *et al.* (2012) indicate that organic contaminants with low octanol-water partition coefficients ($\log K_{ow}$) are difficult to remove by coagulation-sedimentation. Thus, it is reasonable to observe low removal ratios of dissolved QNs by coagulation-sedimentation because $\log K_{ow}$ of the six QNs are less than 3.2. In fact, our previous study (Liu *et al.* 2014) showed that coagulation-sedimentation could only remove 2% of nitrobenzene ($\log K_{ow} = 1.85$) in the presence of *Microcystis aeruginosa*. Although organic contaminants could be adsorbed by sand filter beds, filtration is still inefficient for removing hydrophilic pollutants. In the present study, sand filtration could remove QNs by $2.9 \pm 5.0\%$, which was in accordance with previous studies (Nakada *et al.* 2007; Vieno *et al.* 2007).

It was surprising that ozone-activated carbon filtration in DW-B did not perform a satisfactory capacity for the removal of QNs, though plenty of previous lab-scale studies (Dodd *et al.* 2006; Dewitte *et al.* 2008) indicate that ozonation should be efficient. The competition from natural organic matter may be the key reason. It is reported (Ikehata *et al.* 2008) that other organic or inorganic matter may increase the oxidant requirement and greatly reduce the degradation rate of organic contaminants at trace levels. In DW-B, the TOC was as high as 5 mg/L, which is much higher than the dosages of ozone (usually 0.5 mg/L). The ozone may be quickly consumed by the organic matter in water and then the reaction with QNs is inhibited. Thus, the removal of QNs was limited by the insufficient ozone dosages. This phenomenon implied that the failure of QNs treatment might occur in actual DWTPs if the treatment processes are not properly managed.

4. CONCLUSIONS

In the present study, the occurrence and fate of six species of QNs (SAR, OFL, ENR, CIP, NOR and PIP) in three DWTPs distributed from northeastern to southern China were investigated. The key findings are listed below:

- All of the six selected QNs, SAR, OFL, ENR, CIP, NOR and PIP, were detectable in the raw water of the three DWTPs with total concentrations ranging between 26.4 and 313.8 ng/L.
- After treatment, there was a considerable concentration of dissolved QNs in the finished water with total concentrations of 74.9 ng/L to 148.4 ng/L, and adsorbed QNs were undetectable after the treatment.
- Chemical oxidation, including pre-oxidation and disinfection, was the most efficient method for the removal of dissolved QNs, depending on the chemical structure of QNs and the types of oxidant. ClO_2 is more efficient than chlorine for the removal of OFL and ENR, the dominant QNs in raw water of China.

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CONFLICTS OF INTEREST

There are no conflicts of interest to declare.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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