Effectiveness of conventional wastewater treatment processes in removing pharmaceutically active compounds

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Abstract. Limited work has been done to assess the types and levels of PACs in domestic and treated wastewater in arid and semi-arid countries. In these countries, reuse or artificial recharge of treated sewage effluent is commonly practiced. Thus, the objectives of this study were to quantify the levels of selected PACs in domestic wastewater in the United Arab Emirates (UAE) and to assess the effectiveness of domestic wastewater treatment plants in their removal. An analytical protocol was developed for the analysis of 15 PACs using a UPLC-MS/MS system. Four batches of water and sludge samples were collected from different locations at Al Saad Wastewater Treatment Plant in Al Ain, UAE. Aliquots of each sample were enriched by solid phase extraction. Results show that phenylephrine, dapsone, noscapine, propyl gallate, genistein, and ketoconazole were present in the raw wastewater at low levels (<0.1 µg/L), while acetaminophen and caffeine were present at high levels (>10 µg/L). The overall removal efficiency of the tested PACs from the water stream exceeded 99% for cotinine, acetaminophen, caffeine, naproxen, and ibuprofen, but significantly drops (<50%) for phenylephrine, amoxicillin, dapsone, noscapine, spiramycin, noscapine, genistein and ketoconazole. Analysis of the results indicate that, for highly removed PACs, the main mechanism of removal is possibly aerobic biodegradation. However, for tyramine, dapsone, 9-aminoacridine, noscapine, propyl gallate, and ketoconazole sorption onto the mixed liquor suspended solids first occurs followed by removal by anaerobic digestion. Results of the study should be useful for properly managing treated sewage effluent and sewage sludge.

1. Introduction
Pharmaceutically active compounds (PACs) are found in different environmental systems including surface water [1-3], aquifers [3-6] and soils [7]. These compounds are induced to the environment from various sources such as landfills, agricultural fields, and septic systems. Another significant source is the discharge, use, or artificial recharge of treated sewage effluent (TSE) [8-11]. The presence of these compounds in the TSE is a challenging issue for indirect potable water reuse because of their large number, inability to determine all of them, and the lack of toxicity data for many of them [12]. The frequent incidence of these compounds in natural water systems raises a concern regarding the possibility for them to exist in drinking water [13].

Several investigators studied the occurrence of PACs in raw and treated wastewater [1,2,9,10,14-18]. Comprehensive reviews on the topic have been provided by Verlicchi et al. [19] and Yang et al. [20]. Examples of PACs in the influent and effluent of domestic wastewater treatment plants (WWTPs) along with their range values are listed in Table 1. PACs listed in Table 1 were specifically selected from the literature as they are relevant to this study. Despite the previous effort made in investigating the occurrence of PACs in domestic wastewater, it is difficult to generalize the findings of these studies because of variations in their situational context. Furthermore, limited work...
has been done to assess the types and levels of PACs in domestic wastewater in arid and semi-arid countries. In these countries, reuse or artificial recharge of TSE is commonly practiced. Since soil and aquifer material in these countries have low organic matter content, induced PACs due to reuse or artificial recharge of TSE could pose a higher potential to contaminate aquifers. Thus, the objectives of this study were to quantify the levels of PACs in domestic wastewater in the UAE and to assess the role of wastewater treatment plants in reducing PACs from the waste stream.

| PAC          | Influent | Effluent | Removal Efficiency | Country | Reference |
|--------------|----------|----------|-------------------|---------|-----------|
| Acetaminophen| 1.31-201 | ND       | 0.93-1.0          | Spain   | [14]      |
| Ibuprofen    | 2.28-39.8| ND       | 0.89-0.99         | Spain   | [14]      |
| Naproxen     | 0.27-3.58| ND-0.72  | 0.8-0.89          | Spain   | [14]      |
| Cotinine     | 4.28-27.72| 0.38-9.53| 0.66-0.91         | Spain   | [15]      |
| Phenylephrine| 0.89-4.50| 0.51-1.99| 0.43-0.56         | Spain   | [15]      |
| Caffeine     | 18.31-96.15| 1.21-53.2| 0.45-0.93         | Spain   | [15]      |
| Tyramine     | ND       | ND       | NA                | Spain   | [15]      |
| Dapsone      | ND       | ND       | NA                | Spain   | [15]      |
| 9-Amoxicillin| 0.018    | ND       | NA                | Italy   | [16]      |
| Spiramycin   | 0.603    | 0.375    | 0.38              | Italy   | [16]      |
| Acetaminophen | 55.05-91.28| 0.03-16.72| 0.7-1.0          | USA     | [18]      |
| Ibuprofen    | 11.54-33.25| 0.07-1.69 | 0.85-1        | USA     | [18]      |
| Naproxen     | 6.95-18.39| 0.1-1.45 | 0.79-0.99        | USA     | [18]      |
| Nocapine     | 0.01     | 0.01     | 0              | USA     | [18]      |
| Caffeine     | 73.96-88.33| 0.04-11.65| 0.86-1.0         | USA     | [18]      |
| Cotinine     | 0.82-1.52| 0.01-0.14| 0.85-0.99        | USA     | [18]      |
| Genistein    | 0.025-0.954| 0.009-0.022| 0.64-0.98    | Italy   | [2]       |
| Ketocazoline | 143      | 1.12     | 0.99            | Belgium | [21]      |
| Ibuprofen    | 2.8-25.4 | 0.5-2.6  | 0.82-0.9         | Greece  | [22]      |
| Caffeine     | 17.1-13.2| 1.9-13.9 | 0.88-0.89       | Greece  | [22]      |
| Naproxen     | ND-2.0   | ND-0.7   | 0.48-0.62       | Greece  | [22]      |

Table 1. Range of some PACs (µg/L) in the influent and effluent of domestic WWTPs

a ND means not detected and NA means not available.
b The range represents average values of four WWTPs.

2. Methodology

2.1 Development of analytical protocol

Twenty-three PACs were selected for investigation including aspirin, naproxen, ibuprofen, cotinine, dapsone, amoxicillin, tyramine, phenylephrine, noscapine, spiramycin, propyl gallate, L-ascorbic acid, irgasan, ketoconazole, 9-aminoacridine, genistein, caffeine, estrone, α-estradiol, diethylstilbestrol, equilin, 17α-ethynylestradiol, and estriol. All PACs were purchased from Sigma-Aldrich (purity >99%). Calibration standards that range from 0.05 to 50 mg/L of each PAC were prepared. An analytical protocol was developed for the analysis of the above-mentioned PACs using a UPLC-MS/MS system from Shimadzu (LC-MS 8030). The chromatographic separation was performed on Nexera-i liquid chromatography using a reverse phase column, Discovery C18 HS from Supelico. The mobile phase was made of 90% of 10mM ammonium formate in DI water (pH 2.5) and 10% of methanol: acetonitrile (1:1). The flow rate was 0.6 ml/min and the oven temperature was 40 °C. The UPLC was connected to a triple quadrupole mass spectrometer detector. Both positive and negative electrospray ionization modes were used for ionization of the PACs. A multiple reaction monitoring mode was used for quantification of the target PACs.

Out of the 23 selected PACs, 15 were detected. The instrument detection limit (IDL) for each detected PAC was based on the analysis of 20 replicates of a blank sample. The blank signal at the
retention time of each PAC was recorded and the standard deviation of each was calculated. After that, they were used with the slope ratio between the internal standard and each of the PACs to find the values of the IDL [23].

2.2 Sample collection

Water and sludge samples were collected from Al Saad Wastewater Treatment Plant (WWTP) using glass containers. The plant serves part of Al Ain city, UAE, with a capacity of 92000 m³/day. The plant employs a conventional activated sludge system. Raw wastewater passes first through coarse and fine screens, and then moves to a sand and grease trap unit. Water flows then to primary settling tanks (PST) followed by aeration tanks (divided into aerobic and anoxic zones) where organic matter degradation, nitrification and denitrification take place. After that, water passes to secondary settling tanks (SST). Part of the settled sludge in the SST is recycled to the aeration tanks and the rest flows to anaerobic digesters for further processing followed by mechanical thickening. Water flows from the SST to sand filtration units and finally disinfected by chlorination before being distributed for landscape purposes. A simplified flow sheet diagram of the WWTP is shown in Figure 1. The characteristics of some of the processed waste streams at the plant are tabulated in Table 2.

Four batches of water and sludge samples were collected at different locations on Oct. 10, Oct. 24, Nov. 6, and Nov. 25, 2018. The sampling locations (denoted as 1 to 8 on Figure 1) included raw water, primary settled sludge, processed water after SST, final effluent, recirculated activated sludge, processed sludge after anaerobic digestion, and proceeded sludge after sludge dewatering. Samples collected from locations 1, 3, 4, and 8 are water samples, those from locations 2 and 7 are solids, while those from locations 5 and 6 are sludge. The latter samples were analyzed for PAC content in the aqueous and solid phase separately.

2.3 Sample preparation and analysis

Aliquots of each sample were enriched by solid phase extraction (SPE) (Horizon Technology SPE-DEX® 4790) with HLB-M cartridges from Atlantic. The extracted samples were evaporated until dryness. Before analysis, the dried sample was re-constituted by dissolving it in 0.1 mL of (1:1) mixture of methanol and acetonitrile followed by 0.9 mL of 10 mM ammonium formate buffer. Deuterated cotinine was spiked as an internal standard for loss correction. For water samples, aliquots in 1-L samples were enriched to 1 mL (enrichment factor of 1000). For sludge samples from sampling locations 5 and 6, one liter of each sample was filtered and the separated liquid was reduced to 1 ml by evaporation. Separated solids, as well as solids from sampling locations 2 and 7, were similarly extracted by SPE and the aliquots of each sample were enriched to 1 mL. SPE significantly reduced the method detection limits (MDL) of the PACs.
Table 2. Characteristics of some waste streams and operation parameters at Al Saad WWTP.

| Waste stream                          | Parameter         | Value       |
|---------------------------------------|-------------------|-------------|
| Raw wastewater                        | Flow              | 92000 m³/d  |
|                                       | Suspended solids  | 40204 kg/d  |
| Sludge from primary settling tanks    | Flow              | 503 m³/d    |
|                                       | Suspended solids  | 20102 kg/d  |
| Activated sludge                      | Recirculated flow | 2278 m³/d   |
|                                       | Waste flow        | 832 m³/d    |
|                                       | Suspended solids out | 20298 kg/d |
| Aeration tanks                        | Hydraulic retention time | 4.0 h |
|                                       | Sludge retention time | 5.2 d |
| Final effluent                        | Flow              | 91876 m³/d  |
| Anaerobic digesters                   | Flow              | 832 m³/d    |
|                                       | Suspended solids out | 27710 kg/d |
|                                       | Detention time    | 22 d        |
| Sludge dewatering unit (filter press) | Flow in           | 709 m³/d    |
|                                       | Suspended solids in | 709 kg/d   |
|                                       | Flow out          | 123 m³/d    |
|                                       | Suspended solids out | 27001 kg/d |

3. Results and Discussion

3.1 PACs in raw wastewater

Table 3 lists the concentration of PACs in the raw wastewater for the four collected batches of samples. As shown, for some PACs, the concentration was lower than the MDL in one or more of the batches. The average concentrations and standard deviations were calculated by setting non-detects at the corresponding MDL. The standard deviation values are relatively high, indicating a generally high fluctuation in the concentration among the different batches. However, there is no trend of increase or decrease in the level of PACs during the sampling period. Table 3 shows that phenylephrine, dapsone, noscapine, propyl gallate, genistein, and ketoconazole were present in the raw wastewater at low levels (<0.1 µg/L), while acetaminophen and caffeine were present at high levels (>10 µg/L). The other PACs exist at intermediate levels (i.e., 0.1-10 µg/L).

Table 3. Concentration of PACs (µg/L) in the raw wastewater.

| PAC               | Batch 1 | Batch 2 | Batch 3 | Batch 4 | Average | Standard deviation |
|-------------------|---------|---------|---------|---------|---------|--------------------|
| Phenylephrine     | <0.012  | 0.021   | 0.108   | <0.012  | 0.04    | 0.05               |
| Tyramine          | 0.121   | 0.081   | 1.652   | <0.009  | 0.47    | 0.79               |
| Cotinine          | 5.479   | 3.266   | 4.948   | 2.969   | 4.17    | 1.24               |
| Acetaminophen     | 42.336  | 29.804  | 15.314  | 18.778  | 26.56   | 12.20              |
| Amoxicillin       | <0.522  | 0.629   | <0.522  | <0.522  | <0.522  | 0.55               |
| Caffeine          | 113.478 | 61.285  | 68.010  | 47.714  | 72.62   | 28.52              |
| Dapsone           | 0.050   | 0.096   | 0.088   | 0.040   | 0.07    | 0.03               |
| 9-Aminoacridine   | <0.180  | <0.180  | <0.180  | <0.180  | <0.180  | 0.18               |
| Spiramycin        | <0.016  | 1.467   | <0.016  | <0.016  | <0.016  | 0.38               |
| Noscapine         | 0.028   | 0.034   | 0.028   | <0.006  | 0.02    | 0.01               |
| Propyl gallate    | 0.082   | 0.097   | 0.096   | 0.078   | 0.09    | 0.01               |
| Genistein         | 0.051   | 0.058   | 0.200   | 0.055   | 0.09    | 0.07               |
| Ketoconazole      | 0.109   | 0.083   | <0.007  | <0.007  | <0.007  | 0.05               |
| Naproxen          | 0.864   | 0.135   | 0.490   | 0.905   | 0.60    | 0.36               |
| Ibuprofen         | 2.098   | 0.103   | 1.565   | 4.100   | 1.97    | 1.65               |
The average values of PACs found in this study are generally consistent with the findings of others (see Table 1). For example, Gracia-Lor et al. [14] and Oliveira et al. [18] reported levels of acetaminophen that typically exceeds 10 µg/L. Also, Martínez Bueno et al. [15], Oliveira et al. [18], and Kosma et al. [22] reported levels of caffeine that generally exceeds 20 µg/L. An exception, however, is a higher phenylephrine level reported by Martínez Bueno et al. [15], a higher naproxen level reported by Oliveira et al. [18], and a much higher ketoconazole level reported by Van de Steene and Lambert [21]. Meanwhile, ibuprofen, in our case, is at the lower end of the values reported by others [14,18,22].

3.2 Removal efficiency of PACs

Values of the removal efficiency of PACs following primary settling, secondary treatment (activated sludge system), and filtration and disinfection are listed in Table 4. The removal efficiency values were calculated relative to the concentration in the raw wastewater. The removal efficiency after PST was determined based on mass balance around the PST, while that after the SST and for the FE were determined based on the concentration of PACs at locations 3 and 4 (Figure 1), respectively. In general, primary settling does not play a significant role in removing PACs (Table 4), indicating that the majority of the mass of the PACs is originally present in the liquid phase and not attached to the suspended solids. An exception is a slight removal of caffeine. This is consistent with the finding of others [24-26] who found that the removal of PACs by primary treatment is very poor.

Table 4. Removal of PACs after primary settling tank (RE-PST), secondary settling tank (RE-SST) and final effluent (RE-FE).

| PAC                  | RE-PST (%) | RE-SST (%) | RE-FE (%) |
|----------------------|------------|------------|-----------|
|                      | Min | Max | Ave | Min | Max | Ave | Min | Max | Ave |
| Phenylephrine        | 0.1 | 16.4 | 4.3 | 0.0 | 88.8 | 33.0 | 0.0 | 88.8 | 33.0 |
| Tyramine             | 0.0 | 19.8 | 6.9 | 0.0 | 99.8 | 71.4 | 0.0 | 99.9 | 70.1 |
| Cotinine             | 0.7 | 1.6 | 1.1 | 98.3 | 99.6 | 99.3 | 98.2 | 99.8 | 99.3 |
| Acetaminophen        | 0.0 | 0.2 | 0.1 | 99.7 | 100 | 99.9 | 100 | 100 | 100 |
| Amoxicillin          | 0.4 | 0.5 | 0.4 | 0.0 | 17.1 | 4.3 | 0.0 | 17.1 | 4.3 |
| Caffeine             | 4.5 | 14.4 | 10.5 | 99.6 | 99.8 | 99.8 | 99.8 | 100 | 99.8 |
| Dapsone              | 0.2 | 10.2 | 4.5 | 0.0 | 58.4 | 29.2 | 0.0 | 58.4 | 24.6 |
| 9-Aminoacridine      | 0.4 | 0.5 | 0.5 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| Spiramycin           | 0.0 | 0.4 | 0.3 | 0.0 | 98.9 | 24.7 | 0.0 | 98.9 | 24.7 |
| Noscapine            | 0.5 | 2.0 | 1.3 | 0.0 | 83.4 | 41.7 | 0.0 | 83.4 | 44.2 |
| Propyl gallate       | 0.5 | 1.4 | 0.8 | 17.3 | 98.5 | 71.3 | 98.2 | 98.5 | 98.4 |
| Genistein            | 0.1 | 0.5 | 0.4 | 2.8 | 71.7 | 37.3 | 2.8 | 71.7 | 37.3 |
| Ketoconazole         | 0.0 | 0.5 | 0.2 | 0.0 | 93.4 | 46.2 | 0.0 | 93.4 | 46.2 |
| Naproxen             | 0.0 | 0.0 | 0.0 | 47.4 | 100 | 83.4 | 99.7 | 100 | 99.9 |
| Ibuprofen            | 0.2 | 6.8 | 2.1 | 98.4 | 100 | 99.5 | 98.4 | 100 | 99.5 |

As also shown in Table 4, filtration and disinfection generally do not contribute to the removal of PACs since, for the majority of the PACs, the removal efficiency values at location 3 are almost similar to their corresponding values at location 4. An exception is a slightly improved removal for propyl gallate and naproxen. The poor role of sand filtration in removing PACs is because the filter receives water with low suspended solids that could have sorbed PACs and sand has a quite low sorption ability to dissolved PACs. On the other hand, chlorination is a possible removal mechanism for naproxen [27], but apparently is not important for many other PACs. As such, the main unit operation that affects the removal of the tested PACs is the activated sludge system. However, the removal of the PACs in the activated sludge system varies among the different compounds. For
cotinine, acetaminophen, caffeine, and ibuprofen, the overall removal efficiency values were very high (>99%), but it significantly drops (<50%) for phenylephrine, amoxicillin, dapsone, noscapine, spiramycin, genistein, and ketoconazole. For the other tested PACs (i.e., tyramine, propyl gallate, and naproxen) the removal efficiency by the activated sludge system ranges between 70 and 85%.

For the overall removal of the tested PACs, the removal efficiency was very high (>99%) for cotinine, acetaminophen, caffeine, naproxen, and ibuprofen, high (70-99%) for tyramine and propyl gallate, moderate (30-70%) for phenylephrine, noscapine, genistein, and ketoconazole, and low (<30%) for amoxicillin, dapsone, 9-aminoacridine, and spiramycin. In general, the removal efficiency values for the PACs in this study fall in the range of values reported by others. However, the values for highly removed compounds fall in the upper range of those reported in the literature [14,15,18,21,22], but the removal efficiency values for moderately removed PACs in this study are slightly lower than those reported by others [2,15,16].

3.3 Removal mechanisms of PACs in the activated sludge system

The mass of the PACs that enters the activated sludge system leaves the system either dissolved in clarified water or attached to waste sludge from the SST (shaded area in Figure 1). PACs in the sludge were tested for their levels in the water as well as that on the solid phase. Table 5 lists the average daily mass of PACs leaving the activated sludge system relative to the input mass. The table shows that for highly removed PACs (i.e., cotinine, acetaminophen, caffeine, naproxen, and ibuprofen) the relative mass in the sludge solids is very low (<0.1). This indicates that a major portion of these PACs was removed by transformation reaction. Several transformation reactions could affect the fate of organic pollutants including volatilization, photodegradation, and biodegradation. The consensus, however, is that biodegradation is the main mechanism that affects the removal of PACs in the activated sludge system [19]. The effectiveness of the activated sludge system in removing cotinine, acetaminophen, caffeine, and ibuprofen could be attributed to the operating conditions at the plant which provides sufficient hydraulic retention time (4 h) and sludge retention time (5.2 d) along with the nitrification process employed in the activated sludge system. As indicated by Verlicchi et al. [19] these parameters are important for the cometabolism of PACs in the waste stream.

| PAC                  | Effluent of SST | In sludge water | In sludge solids |
|----------------------|-----------------|-----------------|-----------------|
| Phenylephrine        | 0.699           | 0.022           | 0.042           |
| Tyramine             | 0.303           | 0.012           | 1726            |
| Cotinine             | 0.007           | <0.001          | 0.095           |
| Acetaminophen        | <0.001          | <0.001          | 0.043           |
| Amoxicillin          | 0.960           | 0.030           | 0.056           |
| Caffeine             | 0.003           | <0.001          | 0.103           |
| Dapsone              | 0.796           | 0.035           | 7.3             |
| 9-Aminoacridine      | 1.003           | 0.036           | 15.7            |
| Spiramycin           | 0.754           | 0.769           | 0.046           |
| Noscapine            | 0.685           | 0.024           | 18.4            |
| Propyl gallate       | 0.281           | 0.021           | 4.3             |
| Genistein            | 0.850           | 0.022           | 0.774           |
| Ketoconazole         | 0.540           | 0.023           | 27.7            |
| Naproxen             | 0.001           | 0.004           | <0.001          |
| Ibuprofen            | 0.005           | 0.001           | <0.001          |

The removal of tyramine, dapsone, 9-aminoacridine, noscapine, propyl gallate, and ketoconazole in the activated sludge system appears to be due to accumulation on the mixed liquid suspended solids.
(MLSS) as their relative mass on the solids ranges from about 4 to 1720 (Table 5). Among these compounds, tyramine is the most relatively sorbed one with a mass on the solids that exceeded three orders of magnitude the one in the input water stream. Amoxicillin, spiramycin, and genistein were neither effectively removed from the water nor were they appreciably accumulated on the MLSS.

3.4 Removal of PACs in the anaerobic digester and sludge dewatering system

Figure 2 compares the rate of mass of PACs that enters the anaerobic digester versus the one that leaves the reactor. As indicated above, tyramine, dapsone, 9-aminoacridine, noscapine, propyl gallate, and ketoconazole show accumulation on the MLSS in the activated sludge system. These compounds are significantly removed (92.3-99.9%) in the anaerobic digester (Figure 2). Meanwhile, acetaminophen and caffeine enter the anaerobic digester at relatively high mass (>100 g/d) and they are removed by more than 90%.

Figure 2. Rate of mass of PACs (g/d) as affected by the anaerobic digester and the filter press unit.

Following anaerobic digestion, the sludge is dewatered using a filter press where a cationic polymer (Corofloc 341, SNF, France) is added. Figure 2 compares the rate of the mass of PACs that enters the filter press versus the one that leaves the unit. The mass of PACs that leaves the filter press is the sum of the mass that is adhered to the dewatered sludge (location 7 Figure 1) and the one in the return liquids (location 8 Figure 1). For the majority of the PACs, the mass that leaves the filter press is lower than the one that enters the unit. Although it is not clear what causes this reduction, it could be due to the agglomeration of the solid particles by the polymer or possibly the formation of strong bonds between the polymer and the PACs, making it difficult for the PACs to be released during solid phase extraction.

4. Conclusions

An analytical protocol was developed for the analysis of 15 PACs using a UPLC-MS/MS system equipped with a triple quadrupole mass spectrometer detector. Analysis of water and sludge samples collected from different locations at Al Saad WWTP revealed that acetaminophen and caffeine exist at levels above 10 µg/L in the UAE domestic wastewater. Cotinine, acetaminophen, caffeine, and ibuprofen are highly removed during treatment due to possibly aerobic degradation in the activated sludge system while the moderate removal of tyramine, dapsone, noscapine, and ketoconazole is attributed to accumulation on the MLSS followed by degradation in the anaerobic digesters.
5. References
[1] Ternes T 1998 Water Res. 32, 3245–60.
[2] Bacaloni A, Cavaliere C, Faberi A, Foglia P, Samperì R and Laganà A 2005 Anal. Chim. Acta 531, 229–37.
[3] Meffe R and de Bustamante I 2014 Sci. Total Environ. 481, 280–95.
[4] Lapworth DJ, Baran N, Stuart M. and Ward RS 2012 Environ. Pollut. 163, 287–303.
[5] Grossberger A, Hadar Y, Borch T, Chefetz B 2014 Environ. Pollut. 185, 168–77.
[6] Fram MS and Belitz K 2011 Sci. Total Environ. 409, 3409–17.
[7] Chefetz B, Mualem T and Ben-Ari J 2008 Chemosphere 73, 1335–43.
[8] Kolpin DW, Skopec M, Meyer MT, Furlong ET and Zaugg SD 2004 Sci. Total Environ. 328, 119–30.
[9] Jean J, Perrodin Y, Pivot C, Trepo D, Perraud M, Droguet J, Tissot-Guerraz F and Locher F 2012. J. Environ. Manage. 103, 113–21.
[10] Heberer T 2002 J. Hydrol. 266, 175–89.
[11] Rauch-Williams T, Hoppe-Jones C and Drewes JE 2010 Water Res. 44, 449–60.
[12] Löffler D, Römbke J, Meller M and Ternes TA 2005 Environ. Sci. Technol. 39, 5209–18.
[13] Mompelat S, Le Bot B and Thomas O 2009 Environ. Int. 35, 803–14.
[14] Gracia-Lor E, Sancho JV, Serrano R and Hernández F 2012 Chemosphere 87, 453–62.
[15] Martinez Bueno MJ, Uclés S, Hernando MD and Fernández-Alba AR 2011 Talanta 85, 157–66.
[16] Zuccato E, Castiglioni S, Bagnati R, Melis M and Fanelli R 2010 J. Hazard. Mater. 179, 1042–48.
[17] Wang J and Wang S 2016 J. Environ. Manage. 182, 620–40.
[18] Oliveira TS, Murphy M, Mendola N, Wong V, Carlson D and Waring L 2015 Sci. Total Environ. 518–519, 459–78.
[19] Verlicchi P, Al Aukidy M and Zambello E 2012 Sci. Total Environ. 429, 123–55.
[20] Yang Y, Ok YS, Kim H-H, Kwon EE and Tsang YF 2017 Sci. Total Environ. 596–597, 303–20.
[21] Van de Steene JC and Lambert WE 2008 J. Chromatogr. A 1182, 153–60.
[22] Kosma CI, Lambropoulou DA and Albanis TA 2010 J. Hazard. Mater. 179, 804–17.
[23] Taverniers I, De Loose M and Van Bockstaele E 2004 Trends Anal. Chem. 23, 535-52.
[24] Carballa M, Omil F, Lema JM, Liompart M, Garcia-Jares C, Rodriguez I, Gómez M and Ternes T 2004 Water Res. 38, 2918–26.
[25] Khan SJ and Ongerth JE 2005 Water 32, 80–5.
[26] Zorita S, Martensson L and Mathiasson L 2009 Sci. Total Environ. 407, 2760–70.
[27] Boyd GR, Zhang S and Grimm DA 2005 Water Res. 39, 668–76.

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