International Journal of Earth, Energy and Environmental Sciences
ISSN: 2517-942X
Vol:12, No:6, 2018

Analysis of Pharmaceuticals in Influents of Municipal Wastewater Treatment Plants in Jordan

O. A. Al-Mashaqbeh, A. M. Ghrair, D. Alsafadi, S. S. Dalahmeh, S. L. Bartelt-Hunt, D. D. Snow

***Abstract*—**Grab samples were collected in the summer to characterize selected pharmaceuticals and personal care products (PPCPs) in the influent of two wastewater treatment plants (WWTPs) in Jordan. Liquid chromatography tandem mass spectrometry (LC–MS/MS) was utilized to determine the concentrations of 18 compounds of PPCPs. Among all of the PPCPs analyzed, eight compounds were detected in the influent samples (1,7-dimethylxanthine, acetaminophen, caffeine, carbamazepine, cotinine, morphine, sulfamethoxazole and trimethoprim). However, five compounds (amphetamine, cimetidine, diphenhydramine, methylenedioxyamphetamine (MDA) and sulfachloropyridazine) were not detected in collected samples (below the detection limits <0.005 ng/l). Moreover, the results indicated that the highest concentration levels detected in collected samples were caffeine, acetaminophen, 1,7-dimethylxanthine, cotinine and carbamazepine at concentration of 182.5 µg/L, 28.7 µg/l, 7.47 µg/l, 4.67 µg/l and 1.54 µg/L, respectively. In general, most of compounds concentrations measured in wastewater in Jordan are within the range for wastewater previously reported in India wastewater except caffeine.

***Keywords*—**Pharmaceuticals and personal care products, wastewater, Jordan.

I. Introduction

THE main types of emerging contaminants are PPCPs, endocrine disrupting chemicals (EDCs), plasticisers (e.g. bisphenol-A), flame-retardants, fuel additives and other industrial organic [1]. PPCPs have been detected in all environmental compartments, such as water, soil, air, Biota and in wastewater at concentrations ranging from sub-ng/L levels to µg/L [2], [3]. The presence of these compounds in the environment has been shown to result in adverse ecological and health risks for the exposed biota or humans, even at very low concentrations (ng/L range) [4]-[6].

Municipal WWTPs are considered as a main source for the discharge of PPCPs into surface waters. The literature indicates that currently employed conventional wastewater treatment processes (primary and secondary treatment) cannot effectively eliminate all PPCPs in the raw wastewater [7]-[11]. With an increase in the contamination of waterways and water supply systems from these pollutants and the greater reliance on alternative water sources such as reuse of treated wastewater, it has become apparent that there is a need for further monitoring and research on the impacts of PPCPs on the environment. Recent studies conducted in Europe, USA and Canada have showed that reuse of wastewater effluents (treated and untreated) can result in contamination of ground water and surface water resources by PPCPs [5], [12]-[14]. However, the research efforts made to address this issue in low income countries (i.e. Jordan) is still lag behinds developed countries due to lack of monitoring of PPCPs compounds in water resources as well as lack of availability in the analytical instruments and methods needed to identify PPCPs at low concentration levels (ng/L).

According to a report published in 2017, there are 29 WWTPs operating in different Jordanian cities. The estimated annual amount of treated wastewater discharged by these plant is about 120 Million Cubic Meter (MCM). The problem of emerging contaminants has not received enough attention in Jordan. Very little data are currently available in Jordan on the occurrence and fate of PPCPs in WWTPs.

The objective of this study was to determine some PPCPs compounds in two WWTPs in Jordan during summer season.

II. Materials and Methods

A. Chemicals

Reference materials, metabolites and labeled standards were obtained from Sigma–Aldrich (St. Louis, MO). Solvents used in sample preparation were high-purity grade (OPTIMA, Fisher Scientific, St. Louis, MO).

B. Sample Collection

Grab samples were collected from the influent of As-Samra WWTP on 17/6/2017 and Wadi Al-Seer WWTP 19/6/2017. Grab samples for the analysis of PPCPs were collected in 1 L, rinsed glass bottles and acidified using 1.5 mL hydrochloric acid (HCl, 33%). All samples were stored in a refrigerator under dark conditions at 4 °C to 8 °C.

C. Sample Extractions

The extraction process was implemented according to provided procedure from Water Sciences Laboratory at the University of Nebraska–Lincoln (WSL/UNL) in United State (USA) [15]. Samples were pre-concentrated using solid phase extraction (SPE) directly or within 24 h after collection. The collected samples were firstly decanted to remove suspended particles and then filtered through 0.45 micron glass fiber

Othman A. Al-Mashaqbeh is with the Water and Environment Centre, Royal Scientific Society, Amman. Jordan (corresponding author, e-mail: othman.mashaqbeh@rss.jo).
Ayoup M. Ghrair is with the Water and Environment Centre, Royal Scientific Society, Amman. Jordan
Diya Alsafadi is with the Testing Sector, Royal Scientific Society, Amman. Jordan.
Sahar S. Dalahmeh is with the Department of Energy and Technology, Swedish University of Agricultural Sciences (SLU), Uppsala, Sweden.
Shannon L. Bartelt-Hunt is with the College of Engineering, University of Nebraska–Lincoln, Omaha, USA.
Daniel D. Snow is with the Water Sciences Laboratory, University of Nebraska, Lincoln, USA.

filters using a vacuum filtration unit. A polymeric HLB Oasis 6CC cartridge from Waters (Milford, MA, USA) was connected to a SPE manifold and vacuum pump and preconditioned by passing 6 mL acetone and 6 mL methanol sequentially through the cartridge, followed by 6 mL distilled deionized water (DDI H2O). The filtered sample was then pumped via tube to the cartridge using a vacuum manifold system. The sample flow through the SPE cartridge was kept at ~10mL/min or less. After the whole sample was extracted, the cartridge was rinsed with 5 mL of DDI H2O. Room air was allowed to flow through the cartridge by continued suction for a minimum of five minutes to help dry the cartridge. All cartridges were labeled with necessary information and separately stored in a clean bag at -20°C.

D. Analytical Methods

All extracted samples were then shipped to WSL/UNL for elution and analysis. The pharmaceuticals were analyzed by LC–MS/MS. The pharmaceuticals analysis method used by UNL contains a significant number of compounds [15]. The selected pharmaceutical compounds (18 compounds) and their physical and chemical properties are shown in Table I.

E. Wastewater Plants

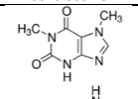
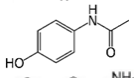
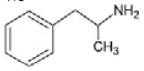
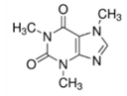
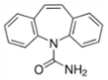
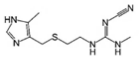
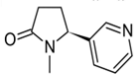
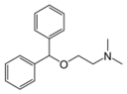
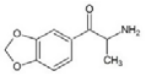
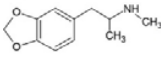
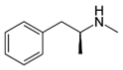
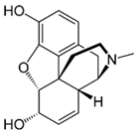
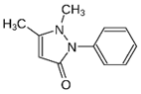
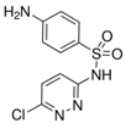
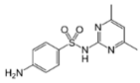
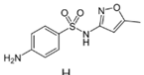
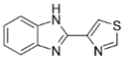
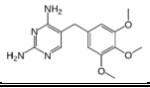
The As-Samra WWTP is considered the largest wastewater treatment facility in Jordan. The design capacity of plant is currently 365,000 m^3 per day using activated sludge/ extended aeration system. The Wadi Al-Seer WWTP is designed to treat an average flow 4000m^3/ day using aerated lagoon treatment method. The As-Samra (WWTP) is located in Zarqa city while the Wadi Al-Seer WWTP is located in Amman. The location of these plants is shown in Fig. 1.

The water samples for this study were collected from the influent after the grit removal unit. The average flow of As-Samra WWTP was 323790 m^3/ day during the sampling period. Both WWTPs are receiving a mixture of domestic, commercial, and industrial wastewater.

II. Results & Discussion

The main pathway for PPCPs discharge into waterways is through WWTP, which are inefficient in removing many of PPCP compounds. The results showed that 12 pharmaceutical compounds were detected in the influent of As-Samra WWTP including 1,7-dimethylxanthine (a metabolite of caffeine), acetaminophen, caffeine, carbamazepine, cotinine, MDMA, morphine, phenazone, sulfamethazine, sulfamethoxazole, thiabendazole and trimethoprim. However, six pharmaceutical compounds were not detected and below the detection limits (<0.005 µg/l) include amphetamine, cimetidine, diphenhydramine, MDA, methamphetamine and sulfachloropyridazine. The eight pharmaceutical compounds detected in the influent of Wadi Alsier WWTP include 1,7-dimethylxanthine, acetaminophen, caffeine, carbamazepine, cotinine, morphine, sulfamethoxazole, and trimethoprim. At this location, 10 pharmaceutical compounds were below the detection limits (<0.005 µg/l) including amphetamine, cimetidine, diphenhydramine, MDA, MDMA, methamphetamine phenazone, sulfamethazine, sulfachloropyridazine and thiabendazole.

TABLE I
Classification and Physical and Chemical Properties of Target Pharmaceuticals

Compound	Chemical structure	Family and use	CAS number
1,7-dimethylxanthine		Stimulant	611-59-6
Acetaminophen		Analgesic	103-90-2
Amphetamine		Stimulant	300-62-9
Caffeine		(CNS) stimulant	*58-08-2*
Carbamazepine		Anticonvulsant	298-46-4
Cimetidine		Antiacid	51481-61-9
Cotinine		Stimulant	486-56-6
Diphenhydramine		Antihistamine	58-73-1
MDA		Abuse drug	101-77-9
MDMA		Abuse drug	42542-10-9
Methamphetamine		Stimulant	51-57-0
Morphine		Narcotic Analgesics	57-27-2
Phenazone		Analgesic	60-80-0
Sulfachloropyradazine		Antibacterial	201-269-9
Sulfamethazine		Antibacterial	57-68-1
Sulfamethoxazole		Antibiotic	723-46-6
Thiabendazole		Fungicide and Parasiticide	148-79-8
Trimethoprim		Antibiotic	738-70-5

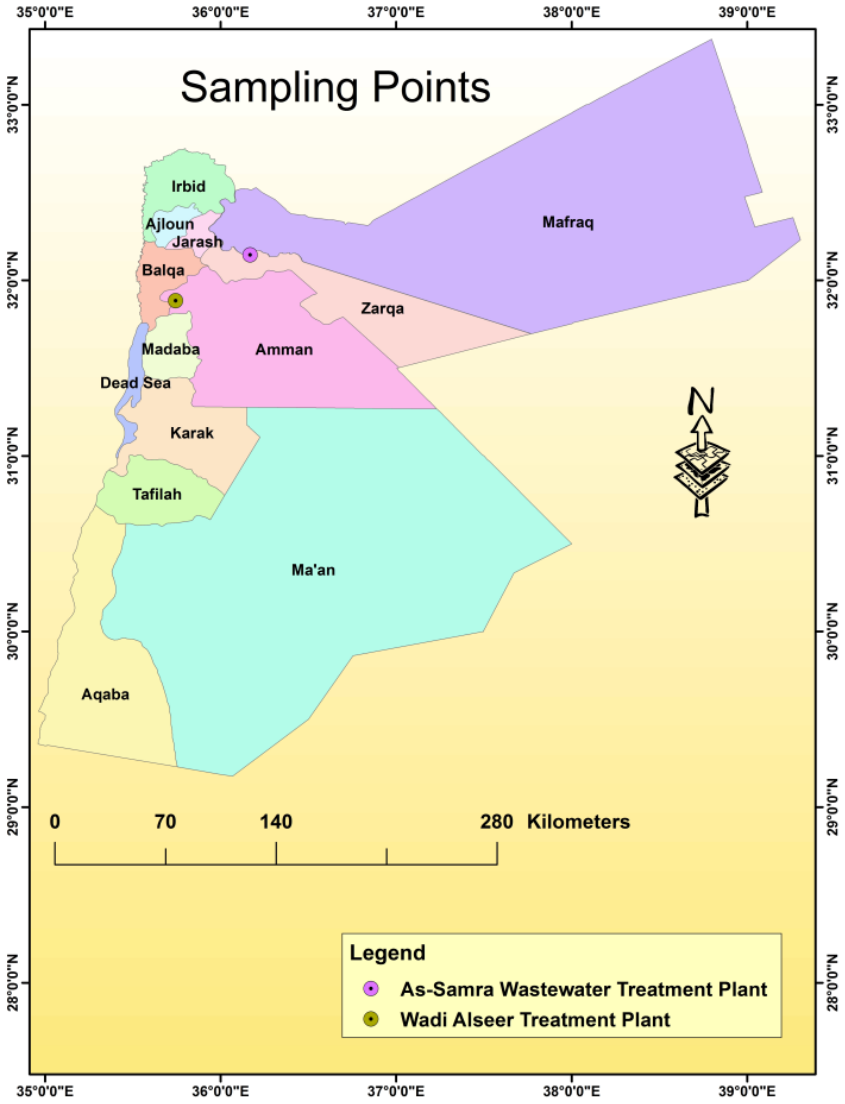


Fig. 1 The location of sampling sites

The concentrations of PPCPs measured in the influent of As-Samra wastewater were generally higher than those in Wadi Alsier WWTP (Table II). This may be due to the large size of the population served by As-Samra WWTP. It is well known that consumption amounts of PPCPs are dependent on the population size. The total population served by As-Samra WWTP is estimated at approximately 2.3 million, whereas Wadi Alsier WWTP population much lower than that (the total population of Wadi Alsier city is about 181,212).

Among PPCPs, the highest concentrations in raw wastewater samples were caffeine, acetaminophen, 1,7-dimethylxanthine, cotinine and carbamazepine at measured concentration of 182.5 µg/L, 28.7 µg/l, 7.47 µg/l, 4.67 µg/l and 1.54 µg/L, respectively. The PPCP compound with the highest estimated concentration is caffeine followed by acetaminophen and the caffeine metabolite 1,7-dimethylxanthine. This is not surprising as caffeine and acetaminophen are available over the counter and used widely.

The concentration of PPCPs entering WWTPs exhibit great variability [16]-[19], [11]. This is mainly due to the large number of variables involved in the behavior and transport of PPCPs from their sources to the WWTP, including fluctuations in consumption patterns and population size served by WWTP. According to a recent review study by Balakrishna et al., 2017 [20]. India is considered as one of the largest drug producers and consumers in the world. This study reported that antibiotics (such as ciprofloxacin) in WTP receiving effluent from drug production as well as amphetamine (illicit drug) from a WTP treating domestic sewer are the highest ever reported from anywhere in the world. Therefore, the concentrations of PPCPs of wastewater at Jordan were compared with 13 pharmaceutical compounds at wastewater in India reported by this review study (Table III). In general, the results showed that most of the compounds concentrations detected in the wastewater in Jordan are within the values reported for wastewater at India. However, the

concentration of caffeine is exceeding these values (Table III).

TABLE II
CONCENTRATIONS OF PHARMACEUTICAL COMPOUNDS DETECTED IN COLLECTED GRAB (PPB) FROM AS-SAMRA WWTP AND WADI ALSIER WWTP

Pharmaceutical Compound	Influent Concentration (ppb) As-Samra WWTP	Influent Concentration (ppb) Wadi Al-Seer WWTP
1,7-Dimethylxanthine	7.47	5.90
Acetaminophen	28.7	0.135
Amphetamine	<0.005	<0.005
Caffeine	182.5	30.0
Carbamazepine	1.54	0.554
Cimetidine	<0.005	<0.005
Cotinine	4.67	0.059
Diphenhydramine	<0.005	<0.005
MDA	<0.005	<0.005
MDMA	0.018	<0.005
Methamphetamine	<0.005	<0.005
Morphine	0.042	0.089
Phenazone	0.042	<0.005
Sulfachloropyridazine	<0.005	<0.005
Sulfamethazine	0.021	<0.005
Sulfamethoxazole	0.349	0.252
Thiabendazole	0.012	<0.005
Trimethoprim	0.128	0.024

TABLE III
COMPARISON OF CONCENTRATIONS OF PHARMACEUTICAL COMPOUNDS (NG/L) BETWEEN WASTEWATER AT JORDAN AND INDIA

Compound	India Concentration range of Influent wastewater	Jordan Concentration range of Influent wastewater
1,7-dimethylxanthine	7,400-19,000	5,909-7,467
Acetaminophen	4,500-86,800	135-28,741
Amphetamine	238-4,720	<5
Caffeine	16-102,840	30,004-182,460
Carbamazepine	22-8,200	554-1,538
Diphenhydramine	34.8-144	<5
MDA	59.2-440	<5-18
MDMA	23	11.5
Methamphetamine	10.4-386	<5
Morphine	141-189	42-89
Sulfamethoxazole	3-2,260	252-349
Thiabendazole	64-123	<5-12
Trimethoprim	3-4,010	24 -128

IV. CONCLUSION

This study tested 18 selected PPCPs in the influent of two WWTP in Jordan. The results showed that 8 pharmaceutical compounds were detected in the collected samples from the influent of As-Samra WWTP and Wadi Alsier WWTP. These compounds are 1,7-dimethylxanthine, acetaminophen, caffeine, carbamazepine, cotinine, morphine, sulfamethoxazole and trimethoprim. However, five pharmaceutical compounds were not detected in both wastewater plants (below the detection limits <0.005 ng/l) include amphetamine, cimetidine, diphenhydramine, MDA and sulfachloropyridazine. Among PPCPs, the highest concentrations in raw wastewater samples were caffeine, acetaminophen, 1,7-dimethylxanthine, cotinine and carbamazepine at measured concentration of 182.4 µg/L, 28.7 µg/l, 7.47 µg/l, 4.67 µg/l and 1.54 µg/L, respectively.

ACKNOWLEDGMENT

The study was supported by the Partnership for Enhanced Engagement in Research (PEER) program administered by the National Academy of Sciences (NAS) and funded by the United States Agency for International Development (USAID), Project number: 5-91 (Cycle 5) “The occurrence and fate of pharmaceutical residues from their sources to water bodies and food chain”. Also, we thank Eng.Sakhaa Al-Naimi and Hanan Hashim for their assistance in sample extraction.

REFERENCES

[1] Daughton, C. G. (2001). "Emerging pollutants, and communicating the science of environmental chemistry and mass spectrometry: Pharmaceuticals in the environment." Journal of the American Society for Mass Spectrometry 12(10): 1067-1076.
[2] Ternes TA (1998) Occurrence of drugs in German sewage treatment plants and rivers. Water Res 32: 3245-3260.doi: 10.1016/S0043-1354(98)00099-3
[3] Kümmerer K. (2009) The presence of pharmaceuticals in the environment due to human use: present knowledge and future challenges. J. Environ. Manage, 8:2354–2358.
[4] Bound, J. P. and N. Voulvoulis (2005). "Household Disposal of Pharmaceuticals as a Pathway for Aquatic Contamination in the United Kingdom." Environmental Health Perspectives.
[5] Kolpin, D. W., E. T. Furlong, M. T. Meyer, E. M. Thurman, S. D. Zaugg, L. B. Barber and H. T. Buxton (2002). "Pharmaceuticals, hormones, and other organic wastewater contaminants in U.S. streams, 1999-2000: A national reconnaissance." Environmental Science and Technology 36(6): 1202-1211.
[6] Bunch, A. and M. Bernot (2011). "Distribution of nonprescription pharmaceuticals in central Indiana streams and effects on sediment microbial activity." Ecotoxicology 20(1): 97-109.
[7] Carballa M, Omil F, Lema JM, Llompart M, García-Jares C, Rodríguez I, et al. Behavior of pharmaceuticals, cosmetics and hormones in a sewage treatment plant. Water Research 2004; 38: 2918-2926.
[8] Jones OA, Lester JN, Voulvoulis N (2005) Pharmaceuticals: a threat to drinking water?. TRENDS in Biotechnology 23: 163-167.
[9] Miège C, Choubert JM, Ribeiro L, Eusèbe M, Coquery M. Fate of pharmaceuticals and personal care products in wastewater treatment plants — conception of a database and first results. Environ Pollut 2009; 157:1721–6.
[10] Monteiro SC, Boxall ABA. Occurrence and fate of human pharmaceuticals in the environment. Rev Environ Contam Toxicol 2010;202:53-154.
[11] Verlicchi P, Al Aukidy M, Zambello E. Occurrence of pharmaceutical compounds in urban wastewater: removal, mass load and environmental risk after a secondary treatment — a review. Sci Total Environ 2012;429:123–55.
[12] Veach, A. M. and M. J. Bernot (2011). "Temporal variation of pharmaceuticals in an urban and agriculturally influenced stream." Science of The Total Environment 409(21): 4553-4563.
[13] Li, H., P. A. Helm and C. D. Metcalfe (2010). "Sampling in the Great Lakes for pharmaceuticals, personal care products, and endocrine-disrupting substances using the passive polar organic chemical integrative sampler." Environmental Toxicology and Chemistry 29(4): 751-762.
[14] Barnes, K. K., D. W. Kolpin, E. T. Furlong, S. D. Zaugg, M. T. Meyer and L. B. Barber (2008). "A national reconnaissance of pharmaceuticals and other organic wastewater contaminants in the United States — I) Groundwater." Science of The Total Environment 402(2–3): 192-200.
[15] Bartelt-Hunt, S. L., D. D. Snow, T. Damon, J. Shockley, and K. Hoagland (2009). The occurrence of illicit and therapeutic pharmaceuticals in wastewater effluent and surface waters in Nebraska.

Environmental Pollution 157(3): 786–791.
[16] Blair, B. et al., 2015. Evaluating the degradation, sorption, and negative mass balances of pharmaceuticals and personal care products during wastewater treatment. *Chemosphere*, 134, pp.395–401. Available at: 227 http://dx.doi.org/10.1016/j.chemosphere.2015.04.078.
[17] Boxall, B. et al., 2014. Exploiting monitoring data in environmental exposure modelling and risk assessment of pharmaceuticals. *Environment International*, 73, pp.176–185. Available at: http://dx.doi.org/10.1016/j.envint.2014.07.018.
[18] Luo, Y. L., Guo, W.S., Ngo, H. H., Nghiem, L. D., Hai, F. I., Zhang, J., Liang, S., Wang, X. C. C. 2014. A review on the occurrence of micropollutants in the aquatic environment and their fate and removal during wastewater treatment. Sci. Total Environ. 473, 619-641.
[19] Verlicchi, P. & Zambello, E., 2015. Pharmaceuticals and personal care products in untreated and treated sewage sludge: Occurrence and environmental risk in the case of application on soil - A critical review. *Science of the Total Environment*, 538, pp.750–767. Available at: http://dx.doi.org/10.1016/j.scitotenv.2015.08.108.
[20] Balakrishna K., Rath A., Praveenkumarreddy Y., Guruge K. S., Subedi B. 2017, A review of the occurrence of pharmaceuticals and personal care products in Indian water bodies. Ecotoxicology and Environmental Safety 137 (2017) 113–120.