

Analysis of Some Pharmaceuticals in Surface Water in Jordan

Othman A, Al-Mashaqbeh¹, Ayoup M. Ghrair¹, Diya Alsafadi², Sahar S. Dalahmeh³, Shannon L. Bartelt-Hunt⁴, Daniel D. Snow⁵

1, Water and Environment Centre, Royal Scientific Society, Amman. Jordan Corresponding Author email: othman.mashaqbeh@rss.jo

2, Testing Sector, Royal Scientific Society, Amman. Jordan

3, Department of Energy and Technology, Swedish University of Agricultural Sciences (SLU), Uppsala, Sweden

4, College of Engineering, University of Nebraska–Lincoln, Omaha, USA

5, Water Sciences Laboratory, University of Nebraska, Lincoln, USA

Abstract:

A quantitative assessment of pharmaceuticals in surface water in Jordan was conducted using liquid chromatography-tandem mass spectrometry (LC-MS/MS) to evaluate the occurrence, source and distribution of 18 pharmaceutical compounds. Grab samples were collected in the summer from the effluent of two dams in Jordan. Among all of the pharmaceuticals analyzed, the results showed that 10 pharmaceutical compounds were detected in the effluent of King Talal Dam including 1,7-dimethylxanthine, acetaminophen, amphetamine, caffeine, carbamazepine, cotinine, phenazone, sulfamethoxazole, sulfamethazine, trimethoprim. However, four pharmaceutical compounds were detected in the effluent of Mujib Dam include 1,7-dimethylxanthine, caffeine, cotinine, phenazone. Moreover, eight pharmaceutical compounds were not detected in both dams ($<0.005 \mu\text{g/l}$) including cimetidine, diphenhydramine, MDA, MDMA, methamphetamine, morphine, sulfachloropyridazine and thiabendazole. The results also indicated that the compound detected at the highest concentration levels in King Talal Dam was carbamazepine at concentration of $0.358 \mu\text{g/l}$. It is very clear that the occurrence of pharmaceuticals at King Talal Dam is higher than in Mujib Dam. This is mainly due to the fact that King Talal Dam is receiving runoff water and treated wastewater from the wastewater treatment plant, while the Mujib Dam is only receiving surface runoff water. This is consistent with many studies reported in the literature that municipal wastewater treatment plants (WWTPs) are considered a primary source for the discharge of pharmaceuticals and personal care products PPCPs into surface waters.

Keywords: Pharmaceuticals and personal care products, surface water, Jordan.

1. Introduction

Jordan's water resources are very vulnerable as the current water consumption has already exceeded its renewable supply. In fact, the deficit between supply and demand is currently covered by over pumping of some of country aquifers causing a massive drop in water table and deteriorating the water quality (Al-Hadidi and Al-Kharabsheh 2015). To resolve the water shortages at Jordan, potential water solutions currently implemented include desalination, reduction water demands, reuse wastewater in the agriculture sector and building dams to harvest surface water.

There are fourteen dams in Jordan with total reservoir capacity of about 336 MCM, including the desert dams. Stored water from these dams is used for drinking water, agriculture activities and groundwater recharge (Ministry of Water and Irrigation, Jordan Valley Authority, 2018). Some of these dams are collecting surface runoff and treated wastewater while other dams are collecting only runoff. As mentioned before, Jordan is reusing treated wastewater. The treated wastewater is discharged from wastewater treatment plants directly to wades and streams and then stored at dam to be used for irrigation. According to the Jordanian Water Authority data, there are 32 wastewater treatment plants (WWTPs) operating in different Jordanian cities in 2018. The estimated annual amount of treated wastewater discharged by these plants is more than 166 Million Cubic Meter (MCM).

It is well known in the literature that conventional WWTPs are not designed to remove emerging pollutants such as pharmaceuticals (Díaz-Garduño et al., 2017). Most of these low-level contaminants can pass the WWTPs and eventually reaching surface water and groundwater (Lapworth et al., 2012; Lopez-Doval et al., 2017). Recent studies conducted in Europe, USA and Canada have shown that reuse of wastewater effluents (treated and untreated) can result in contamination of ground water and surface water resources by pharmaceuticals (Kolpin et al, 2002, Veach and Bernot, 2011, Li et al, 2010, Barnes et al, 2008). The literature indicates that effluent from municipal wastewater treatment plants (WWTPs) is the main source for the discharge of pharmaceuticals into surface waters. A recent study showed that treated wastewater in Jordan is contaminated by some pharmaceutical compounds such as caffeine (182.5 µg/L), acetaminophen (28.7 µg/l), 1,7-dimethylxanthine (7.47 µg/l), cotinine (4.67 µg/l) and carbamazepine (1.54 µg/L) (Al-Mashaqbeh et al., 2018).

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 pharmaceutical compounds carried by treated wastewater on the surface water. However, the research efforts made to address this issue has not received enough attention in Jordan. Therefore, very little data are currently available on the occurrence and fate of pharmaceutical compounds in water dams in Jordan.

The objective of this study was to determine some pharmaceutical compounds in King Talal dam and Mujib dam in Jordan during summer season.

2. Materials and methods

2.1. 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).

2.2. Sample collection:

Grab samples were collected from the effluent of King Talal dam on 17/6/2017 and Mujib dam on 19/6/2017. Grab samples for the analysis of pharmaceutical compounds 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 to 8 °C.

2.3. Sample Extraction

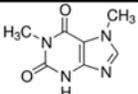
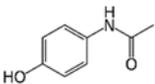
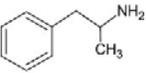
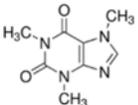
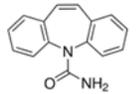
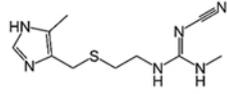
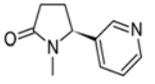
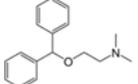
The extraction process was implemented according to provided procedure from Water Sciences Laboratory at the University of Nebraska–Lincoln (WSL/UNL) in United States (USA) and included pharmaceuticals from a previous study (Bartelt-Hunt et al. 2009). Samples were pre-concentrated using solid phase extraction (SPE) within 24 h after collection. The collected samples were firstly decanted to remove suspended particles and then filtered through 0.45 micron glass fiber filters using a vacuum filtration unit. A 500 mg 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

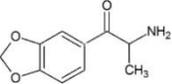
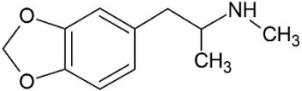
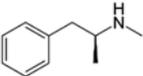
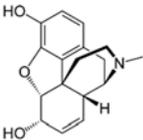
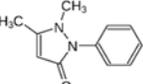
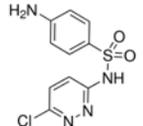
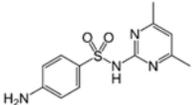
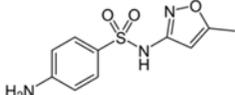
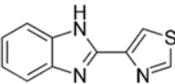
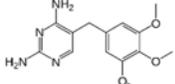
with 5 mL of DDI H₂O. Room air was allowed to flow through the cartridge by continued suction for a minimum of five minutes to help dry the cartridge. All cartridges were labeled with necessary information and separately stored in a clean bag at -20°C.

2.4. Analytical methods

All extracted samples were then shipped to WSL/UNL for elution and analysis. The pharmaceuticals were analyzed by liquid chromatography and tandem mass spectrometry (LC-MS/MS). The pharmaceuticals analysis method used by UNL contains a significant number of compounds (Bartelt-Hunt et al.2009). The selected pharmaceutical compounds (18 compounds) and their physical and chemical properties are shown in Table 1.

Table 1: 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

2.5. Surface water dams:

King Talal Dam (KTD) is located in Amman-Zarqa basin (AZB) which comprises several cities (Amman, Zarqa, Mafraq, Jerash and Balqa). The reservoir receives drainage from most of the watershed in AZB (Figure 1). The total area of the basin 3860 km² where around 95% of the area is within Jordan and 5% is in Syria reaching to the Syrian city of Salkhad in Jebal al-Arab the Syrian borders. The Zarqa river is the main watercourse passing through AZB and discharge into KTD. (Figure 1). KTD is currently receiving surface flow including surface runoff from AZB and treated wastewater discharged by the four wastewater treatment plants (As Samra, Al-Baqa, Abu

Nusair and Jarash). Therefore, KTD water is being only used for agriculture activities in Jordan valley.

Mujib dam is located in southern Jordan at Mujib basin (90 kilometres south of Amman). The Mujib watershed covers an area of 6571.4 km². It comprises two major tributaries: the northern tributary, termed Wadi Wala (2063.6 km²), and the southern tributary, known as Wadi Mujib (4507.8 km²). The both tributaries are merge 3 km before the Wadi discharges into the Dead Sea. Five dams have been constructed across the catchment. The most important is Mujib dam with a capacity of 16.8 MCM per year. The Mujib dam is currently receiving only surface runoff from Mujib catchment. Therefore, its water quality is being used for drinking supplies water for the southern Ghor and Amman. The water samples for this study were collected from the discharge of dam.

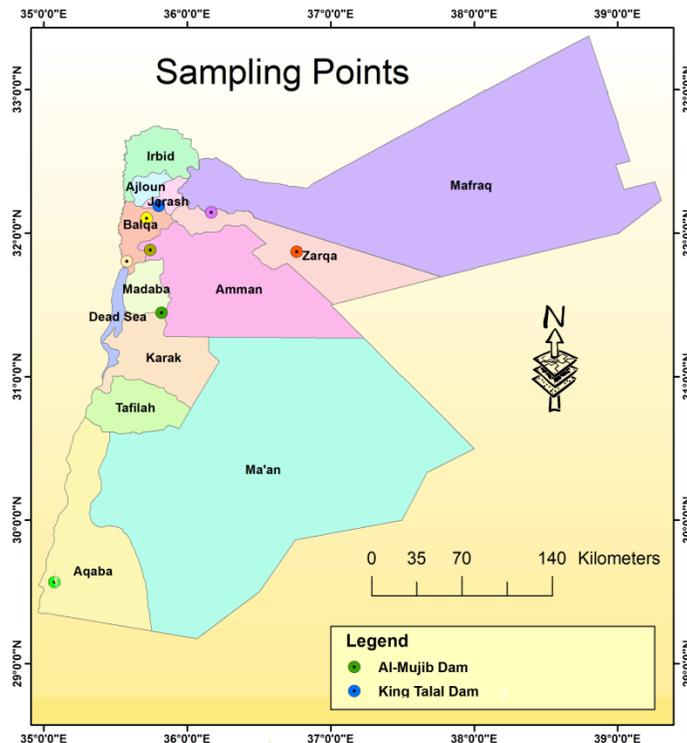


Figure 1: The location of sampling sites.

3. Results & Discussion

The results show that ten pharmaceutical compounds were detected in the effluent of KTD including 1,7-dimethylxanthine (a metabolite of caffeine), acetaminophen, amphetamine, caffeine, carbamazepine, cotinine, phenazone, sulfamethoxazole, sulfamethazine, trimethoprim. However, eight pharmaceutical compounds were not detected and below the detection limits ($<0.005 \mu\text{g/l}$) include cimetidine, diphenhydramine, MDA, MDMA, methamphetamine, morphine, sulfachloropyridazine and thiabendazole. In Mujib dam, the results showed that four pharmaceutical compounds were detected in the effluent of Al-Mujeb Dam include 1,7-dimethylxanthine, caffeine, cotinine, phenazone, Moreover, fourteen pharmaceutical compounds were below the detection limits ($<0.005 \mu\text{g/l}$) including acetaminophen, amphetamine, carbamazepine, cimetidine, diphenhydramine, MDA, MDMA, methamphetamine, morphine, sulfachloropyridazine, sulfamethoxazole, sulfamethazine, thiabendazole, and trimethoprim.

Table 2: Concentrations of pharmaceutical compounds detected in collected grab samples ($\mu\text{g/l}$) from King Talal Dam and Mujib Dam.

Pharmaceutical Compound	King Talal Dam (KTD) Effluent Concentration ($\mu\text{g/l}$)	Mujib Dam Effluent Concentration ($\mu\text{g/l}$)
1,7-Dimethylxanthine	0.053	0.010
Acetaminophen	0.036	<0.005
Amphetamine	0.018	<0.005
Caffeine	0.076	0.089
Carbamazepine	0.358	<0.005
Cimetidine	<0.005	<0.005
Cotinine	0.015	0.015
Diphenhydramine	<0.005	<0.005
MDA	<0.005	<0.005
MDMA	<0.005	<0.005
Methamphetamine	<0.005	<0.005
Morphine	<0.005	<0.005
Phenazone	0.059	0.050
Sulfachloropyridazine	<0.005	<0.005
Sulfamethazine	0.041	0.008
Sulfamethoxazole	0.039	<0.005
Thiabendazole	<0.005	<0.005

Trimethoprim

0.015

<0.005

For KTD, the results showed that carbamazepine was the pharmaceutical present at the highest concentration levels 0.358 $\mu\text{g/l}$, followed by caffeine 0.076 $\mu\text{g/l}$, phenazone 0.059 $\mu\text{g/l}$, 1,7-Dimethylxanthine 0.053 $\mu\text{g/l}$, sulfamethazine 0.041 $\mu\text{g/l}$, sulfamethoxazole 0.039 $\mu\text{g/l}$, acetaminophen 0.036 $\mu\text{g/l}$, amphetamine 0.018 $\mu\text{g/l}$, cotinine 0.015 $\mu\text{g/l}$, trimethoprim 0.015 $\mu\text{g/l}$. However, for Mujib dam, caffeine was the highest concentration levels 0.089 $\mu\text{g/l}$, followed by phenazone 0.050 $\mu\text{g/l}$, cotinine 0.015 $\mu\text{g/l}$ and 1,7-dimethylxanthine 0.010 $\mu\text{g/l}$.

The concentrations of PPCPs measured in the effluent of KTD were generally higher than those in Mujib dam (Table 2). It is well known that KTD is one of the most polluted reservoir in Jordan. This is mainly due to many pollution sources exist at AZB such as the wastewater treatment effluents, the effluents from industries, overflows from broken septic tanks pipelines, inefficient drainage system, domestic waste. In addition, there are several public and private hospitals, clinics, and medical analysis laboratories located AZB. Moreover, it is well known that As-Samra Wastewater Treatment Plant (WWTP) is the largest wastewater treatment facility in Jordan which is located at AZB. It is annually discharging about 100MCM of treated wastewater to Zarqa river and finally stored at KTD. A recent study has showed that the levels detected in collected samples from the effluent of As-Samra WWTP were caffeine, acetaminophen, 1,7-dimethylxanthine, cotinine and carbamazepine at concentration of 182.5 $\mu\text{g/l}$, 28.7 $\mu\text{g/l}$, 7.47 $\mu\text{g/l}$, 4.67 $\mu\text{g/l}$ and 1.54 $\mu\text{g/l}$, respectively (Al-Mashaqbeh et al., 2018). The analysis of surface water samples at KTD reveals the persistent presence of pharmaceutical compounds in KTD water with the same distribution as in effluent samples from As-Samra WWTP. It is likely that WWTPs operating at AZB watersheds do not properly remove pharmaceutical compounds, ultimately form the main source of pharmaceutical compounds to this important aquatic ecosystem. On the other hand, the low concentration levels of pharmaceutical compounds found in Mujib dam can be explained because of the fact that its location relatively far with respect to the other industrial activities and

also because of the relatively scarce number of wastewater treatment plants in its surrounding catchment.

Overall, all of selected pharmaceuticals compounds were detected along the KTD dam and Mujib dam indicating that the continuous output of treated wastewater, urban runoff is among the sources that lead to the presence of pharmaceutical residues along the surface water. The KTD Dam is a valuable water source used for irrigating crops, hence the presence of PPCPs may have an effect on the quality and grade of vegetables grown in the region.

The concentrations of detected pharmaceuticals in this study were compared with those reported in previous studies globally as presented in Table 3. In general, the targeted pharmaceuticals in the current study are comparable with reported data and within the range reported by the literature on pharmaceutical present in surface water worldwide except for carbamazepine.

Table 3: Comparison of concentrations of pharmaceutical compounds (ng/L) between surface water at Jordan and worldwide.

Compound	location	Worldwide Concentration (ng/L)	This study Concentration (ng/L)	Reference
1,7-dimethylxanthine	Lake Michigan- USA	25-75	10-53	Ferguson et al., (2013)
Acetaminophen	Lake Michigan- USA	2.5-17	<5-36	Ferguson et al., (2013)
Amphetamine	Pearl river- China	17.4-58.2	<5-18	Li et al.,(2016)
Caffeine	Lake Michigan- USA	18-100	76-89	Ferguson et al., (2013)
Carbamazepine	Lake Michigan- USA	0.5-10	<5-358	Ferguson et al., (2013)
Cotinine	Lake Michigan- USA	1.5-11	15	Ferguson et al., (2013)
Phenazone	Czech. Rep., Germany	35- 2500	50-59	Roig, (2010)

Sulfamethazine	Lake Michigan- USA	0.5-1.5	8-41	Ferguson et al., (2013)
Sulfamethoxazole	Lake Michigan- USA	1.5-220	<5-39	Ferguson et al., (2013)
	Selangor River - Malaysia	84.31-114.24		Praveena et al.,(2018)
Trimethoprim	Lake Michigan- USA	2.5-18	<5-15	Ferguson et al., (2013)

4. Conclusion:

Within this study, 18 pharmaceutical compounds were screened in the water samples collected from KTD and Mujib dam to evaluate the influence of discharging treated wastewater to surface water. The results revealed that KTD detected more pharmaceutical compounds compared to Mujib dam. The results showed that ten pharmaceutical compounds (1,7-dimethylxanthine, acetaminophen, amphetamine, caffeine, carbamazepine, cotinine, phenazone, sulfamethoxazole, sulfamethazine, trimethoprim) were detected in the effluent of King Talal Dam, while four pharmaceutical compounds 1,7-dimethylxanthine, caffeine, cotinine, phenazone detected at Al-Mujb Dam. Among the detected compounds at KTD, Carbamazepine was the pharmaceutical present at the highest concentration levels 0.358 µg/l, while Caffeine was the highest concentration 0.089 at Mujib dam. The number of detected pharmaceuticals in KTD were distinctly higher than in Mujib dam, suggesting that treated wastewater discharged by wastewater treatment plants might be the major source of the increase of these pharmaceuticals in the KTD. The results showed that the contamination of KTD water by carbamazepine are certainly related to treated wastewater discharged by wastewater treatment plants in Zarqa river. The study points out the need for continuous monitoring of contamination levels not only in the KTD but also in other major Jordanian dams which are receiving treated wastewater.

5. Acknowledgments:

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