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Analysis of some pharmaceuticals in surface water in Jordan

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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 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 μg/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 μg/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 (WWTP), while the Mujib Dam is only receiving surface runoff water. This is consistent with many studies reported in the literature that municipal WWTPs are considered a primary source for the discharge of pharmaceuticals and personal care products 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 had already exceeded its renewable supply. In fact, the deficit between supply and demand is currently covered by over pumping of some of the country's 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 14 dams in Jordan with total reservoir capacity of about 336 million cubic meter (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 (WWTPs) 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 WWTPs operating in different Jordanian cities in 2018. The estimated annual amount of treated wastewater discharged by these plants is more than 166 MCM.

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It is well known in the literature that conventional WWTPs are not designed to remove emerging pollutants such as pharmaceuticals (Díaz-Gardu~no et al., 2017). Most of these low-level contaminants can pass the WWTPs and eventually reach surface water and groundwater (Lapworth et al., 2012; Lopez-Doval et al., 2017). Recent studies conducted in Europe, the 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 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 of 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°C 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 the United States 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 first 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 H_2O). 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 ~10 mL/min or less. After the whole sample was extracted, the cartridge was rinsed with 5 mL of DDI H_2O. Room air was allowed to flow through the cartridge by continued suction for a minimum of 5 min 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.

2.5. Surface water dams

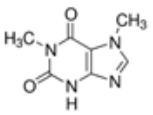
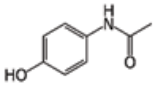
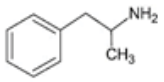
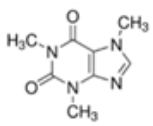
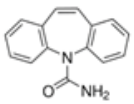
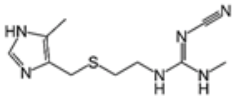
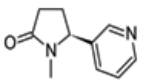
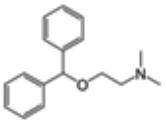
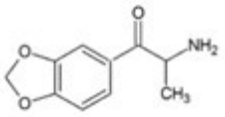
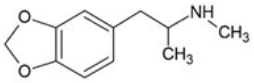
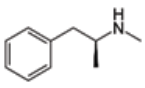
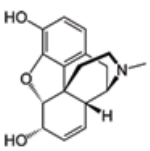
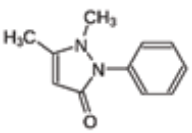
King Talal Dam (KTD) is located in Amman-Zarqa basin (AZB) which comprises several cities (Amman, Zarqa, Mafraq, Jerash and Balqa). The reservoir receives drainage from most of the watershed in AZB (Fig. 1). The total area of the basin is 3,860 km^2 where around 95% of the area is within Jordan and 5% is in Syria reaching to the Syrian city of Salkhad in Jebal al-Arab the Syrian boarders. The Zarqa river is the main watercourse passing through AZB and discharge into KTD (Fig. 1). KTD is currently receiving surface flow including surface runoff from AZB and treated wastewater discharged by the four WWTPs (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 km south of Amman). The Mujib watershed covers an area of 6,571.4 km^2. It comprises two major tributaries: the northern tributary, termed Wadi Wala (2,063.6 km^2), and the southern tributary, known as Wadi Mujib (4,507.8 km^2). Both tributaries 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.

3. Results and discussion

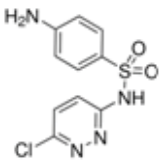
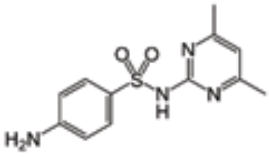
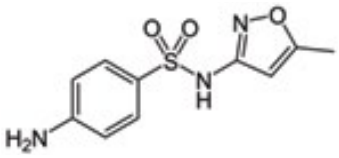
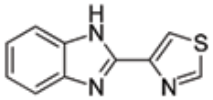
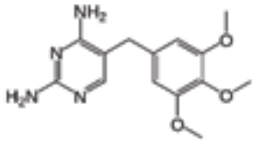
The results show that 10 pharmaceutical compounds were detected in the effluent of KTD including 1,7-dimethylxanthine (a metabolite of caffeine), acetaminophen,

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		Antacid	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

Ccontinued)

Table 1–*(Continued)*

Compound	Chemical structure	Family and use	CAS number
Sulfachloropyridazine		Antibacterial	201-269-9
Sulfamethazine		Antibacterial	57-68-1
Sulfamethoxazole		Antibiotic	723-46-6
Tiabendazole		Fungicide and parasiticide	148-79-8
Trimethoprim		Antibiotic	738-70-5

amphetamine, caffeine, carbamazepine, cotinine, phenazone, sulfamethoxazole, sulfamethazine, trimethoprim. However, eight pharmaceutical compounds were not detected and below the detection limits (<0.005 μg/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 including 1,7-dimethylxanthine, caffeine, cotinine, phenazone, Moreover, 14 pharmaceutical compounds were below the detection limits (<0.005 μg/L) including acetaminophen, amphetamine, carbamazepine, cimetidine, diphenhydramine, MDA, MDMA, methamphetamine, morphine, sulfachloropyradazine, sulfamethoxazole, sulfamethazine, thiabendazole, and trimethoprim.

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

The concentrations of pharmaceuticals and personal care products (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 existence of several pollution sources at AZB such as wastewater treatment effluents, 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 WWTP is the largest wastewater treatment facility in Jordan which is located at AZB. It is annually discharging about 100 MCM 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, 28.7, 7.47, 4.67 and 1.54 μg/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 is relatively far from other industrial activities and also because of the relatively scarce number of WWTPs in its surrounding catchment.

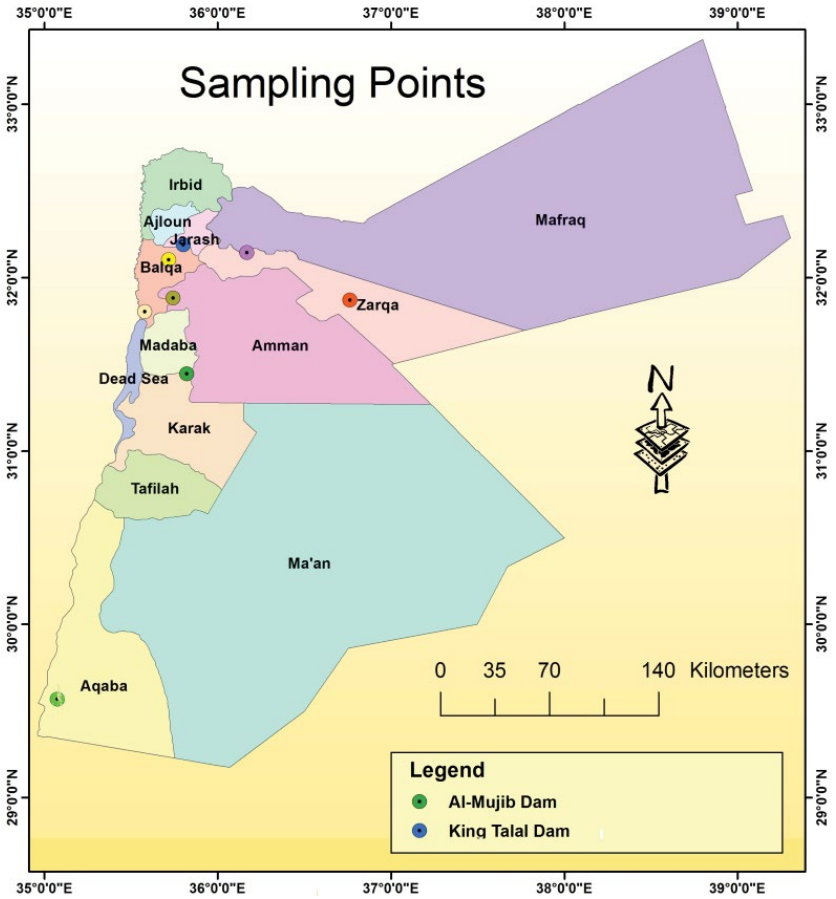


Fig. 1. Location of sampling sites.

Table 2
Concentrations of pharmaceutical compounds detected in collected grab samples (μg/L) from King Talal Dam and Mujib Dam

Pharmaceutical compound	King Talal Dam (KTD) effluent concentration (μg/L)	Mujib Dam effluent concentration (μg/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

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 Republic, Germany	35–2,500	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)

Overall, all of selected pharmaceuticals compounds were detected along the KTD and Mujib Dam indicating that the continuous output of treated wastewater, urban run-off is among the sources that lead to the presence of pharmaceutical residues along the surface water. The KTD is a valuable water source used for irrigation, 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.

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 with Mujib Dam. The results showed that 10 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 were 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 in Mujib Dam, caffeine was present at the highest concentration levels 0.089. The number of detected pharmaceuticals in KTD was distinctly higher than in Mujib Dam, suggesting that treated wastewater discharged by WWTPs 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 is certainly related to treated wastewater discharged by WWTPs 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.

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References

Al-Hadidi, M., Al-Kharabsheh, A. (2015). Effect of Over pumping on Water Quality Deterioration in Arid Areas: A Case Study of Dead Sea Basin/Jordan, Jordan Journal of Agricultural Sciences, Volume 11, No. 1, University of Jordan, Amman, Jordan.

Díaz-Gardu~no, B., Pintado-Herrera, M.G., Biel-Maeso, M., Rueda-Martínez, J.J., Lara-Martín, P.A., Perales, J.A., Manzano, M.A., Garrido-P_erez, C., Martín-Díaz, M.L., 2017. Environmental risk assessment of effluents as a whole emerging contaminant: efficiency of alternative tertiary treatments for wastewater depuration. Water Res. 119, 136e149.

Lapworth, D., Baran, N., Stuart, M., Ward, R., 2012. Emerging organic contaminants in groundwater: a review of sources, fate and occurrence. Environ. Pollut. 163, 287e303.

Lopez-Doval, J.C., Montagner, C.C., de Albuquerque, A.F., Moschini-Carlos, V., Umbuzeiro, G., Pompeo, M., 2017. Nutrients, emerging pollutants and pesticides in a tropical urban reservoir: spatial distributions and risk assessment. Sci. Total Environ. 575, 1307e1324. https://doi.org/10.1016/j.scitotenv.2016.09.210.

Al-Mashaqbeh, O. A., Ghrair, A. M., Alsafadi, D., Dalahmeh, S. S., Bartelt-Hunt, S. L., Snow D. D. (2018). Analysis of Pharmaceuticals in Influents of Municipal Wastewater Treatment Plants in Jordan. World Academy of Science, Engineering and Technology. Int. J. Environ. Ecol. Eng. Vol: 12, No: 6.

Kolpin, D. W., Furlong, E. T., Meyer, M. T., Thurman, E. M., Zaugg, S. D., Barber, L. B., Buxton, H. T. (2002). Pharmaceuticals, hormones, and other organic wastewater contaminants in U.S. streams, 1999–2000: A national reconnaissance. Environ. Sci. Technol., 36(6), 1202–1211.

Veach, A. M., Bernot, M. J. (2011). Temporal variation of pharmaceuticals in an urban and agriculturally influenced stream. Sci. Total Environ., 409(21), 4553–4563.

Li, H., Helm, P. A., Metcalfe, C. D., (2010). Sampling in the Great Lakes for pharmaceuticals, personal care products, and endocrine-disrupting substances using the passive polar organic chemical integrative sampler. Environ. Toxicol. Chem. 29(4), 751–762.

Barnes, K. K., Kolpin, D. W., Furlong, E. T., Zaugg, S. D., Meyer, M. T., Barber, L. B. (2008). A national reconnaissance of pharmaceuticals and other organic wastewater contaminants in the United States — I) Groundwater. Sci. Total Environ., 402(2–3), 192–200.

Bartelt-Hunt, S. L., Snow, D. D., Damon, T., Shockley, J., Hoagland, K. (2009). The occurrence of illicit and therapeutic pharmaceuticals in wastewater effluent and surface waters in Nebraska. Environ. Pollut. 157(3), 786–791.

Ferguson, P.J., Bernot, M.J., Doll, J.C., Lauer, T.E. (2013). Detection of pharmaceuticals and personal care products (PPCPs) in near-shore habitats of southern Lake Michigan, Sci. Total Environ., 458–460, 187–196.

Li, K., Du, P., Xu, Z., Gao, T. Li, X. (2016). Occurrence of illicit drugs in surface waters in China. Environ. Pollut., 213, 395–402.

Roig B, editor (2010). Pharmaceuticals in the Environment: Current knowledge and need assessment to reduce presence and impact. London, UK: IWA publishing.

Praveena, S., Shaifuddin, S., Sukiman, S., Nasir, F., Hanafi, Z., Kamarudin, N., Ismail, T., Aris, A. (2018). Pharmaceuticals residues in selected tropical surface water bodies from Selangor (Malaysia): Occurrence and potential risk assessments. Sci. Total Environ., 642, 230–240.