Determination of aspirin in municipal wastewaters of Nur-Sultan City, Kazakhstan

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Abstract. The presence of aspirin in the municipal wastewater of Nur-Sultan city, Kazakhstan, was studied in this research. Aqueous phase samples were collected before any treatment [1] and in the end of treatment process of Nur-Sultan wastewater treatment plant [2]. The study was conducted from April to December 2021. The concentrations of target compound were measured using high-pressure liquid chromatography (HPLC).
The obtained results showed that the concentration of aspirin was generally higher than those reported in the literature. For instance, influent and effluent concentrations of aspirin were equal to 42.8 – 60.4 ppb and 1.4 – 6.5 ppb, respectively (October – December period). The removal of aspirin by wastewater treatment process was equal to 50 - 90.2%. Aspirin was not detected in the spring-summer period of 2021. This could be due to usage of aspirin as a medicine for the treatment and prevention of seasonal flu in the autumn-winter period by the population of the city of Nur-Sultan. Currently, our research team is working on investigation of other potential contaminants of emerging concern in municipal wastewaters of Nur-Sultan city and on treatment methods that could efficiently remove the contaminants of emerging concern.

1. Introduction

Pharmaceuticals have recently attracted the attention of the international scientific community as a new class of potential environmental concerns. They are new environmental pollutants actively consumed by the population [1,2]. Many of them are stored in the human body and are often excreted into the environment unchanged. In many countries, they have been found in low concentrations in various

environmental objects, like effluent from wastewater treatment plants, surface, sea, and ground waters [3–8]. Depending on consumption patterns and population size, the number of pharmaceuticals delivered to wastewater treatment plants may fluctuate in different countries [9].

In the scientific literature, there is little data on the fate of pharmaceuticals in the environment and the mechanism of their action on living organisms. Many pharmaceuticals are highly resistant to environmental factors and often disseminate through the aquatic environment and through the food chain [10]. At wastewater treatment facilities, pharmaceuticals are exposed to ultraviolet radiation, activated sludge, hydrolysis, adsorption and, as a result, return to the environment either as the parent compound or as a metabolite.

Degradation of by-products is another concern, as their toxicity may be the same as or greater than that of the parent compounds [10–14]. According to the statistics, non-steroidal anti-inflammatory medicines (NSAIDs) are the most encountered pharmaceutical contaminants in the environment. Acetylsalicylic acid (aspirin) - non-steroidal anti-inflammatory, antirheumatic drug is a common contaminant [6,8]; chemically, it is 2-acetoxybenzoic acid [15–17]. In addition, acetylsalicylic acid is available and widely used as an analgesic, antipyretic, and blood clots preventer [18–20]. Many authors use HPLC to determine aspirin in various media, including organic liquids [21], although, according to [22], this method is not always highly sensitive.

The incentive for ongoing study on these drugs is the interest generated by the need to monitor drugs in effluents from municipal wastewater treatment plants. In Kazakhstan, there are no officially published data on the results of experimental analytical determination and the content of any drug in waste- and surface waters. The presence of drugs in wastewaters of concern associated with the entry of the contaminants of emerging concern into the environment. Any entry of drugs may lead to risks associated with future environmental problems, like negative effects on environment, human/fauna health, etc. Since municipal wastewater treatment plants have been identified as the main sources of pharmaceutical releases to the aquatic environment, this work is aimed at studying and evaluating aspirin concentrations in effluents from the municipal wastewater treatment plant in Nur-Sultan, Kazakhstan.

Out of the 40 reservoirs available in the region for guaranteed water supply, the flows of the Yesil River are regulated by three of them, one of which is the Vyacheslav reservoir. The Vyacheslav reservoir is intended for water supply to the city of Nur-Sultan, irrigation, as well as for the Yesil River sanitation [23].

The growth and development of the capital of Kazakhstan - Nur-Sultan - has increased anthropogenic influence on the Yesil River, enhancing its recreational value. These factors require strict environmental monitoring and systematic assessment of the ecological status of the river. Nur-Sultan sity is characterized by relative density of a growing population and developed infrastructure. Water is used in both centralized and decentralized manner for household and drinking purposes. It is assumed that the impact of both agriculture and household sector is accompanied by pollution of surface waters with wastewater and surface run-off from the catchment area of reservoirs [24]. Therefore, monitoring of the Yesil River's ecological state is an urgent task.

The sewage treatment plant site at Nur-Sultan is located on the left bank of the Yesil River, approximately 6.5 kilometres southwest of city itself. The project of city's wastewater treatment facility has been developed in accordance with modern technology. It includes four stages of wastewater treatment: mechanical treatment, settling, biological treatment, and UV disinfection.

This decision allowed treated wastewater to be discharged into the Yesil river to replenish water losses caused by its intake from the Vyacheslav reservoir. Wastewater is thus transformed back into raw water as it passes through the river.

Pharmaceutical compounds enter the environment mainly through municipal wastewater [33]. The percentage of removal described in the literature varies and appears to depend on the treatment plant. The

removal efficiency of various medicines in wastewater treatment plants ranged from 13% to 100% in summer and from 0.88% to 99% in winter. However, many researchers consider wastewater treatment at stations insufficient to remove all drugs [25].

Based on extensive literature review, technologies proposed to improve the performance of wastewater treatment plants include accelerated oxidation [35], photocatalytic process [26,27], and medicine sorption on the precipitate, which occurs through absorption and adsorption and can help improve medicine removal efficiency [28–32]. Technologies for removing acetylsalicylic acid from water are under study. To remove aspirin from water, various authors suggest using membrane technologies, activated carbon in combination with clay [3], and sunlight in the presence of a photocatalyst based on a titanium dioxide polymer film [5]. The authors believe that these technologies are the most efficient [33,34].

This work was focusing on influent and effluent concentrations of aspirin and treatment capability of the wastewater treatment plant of Nur-Sultan city, Kazakhstan. The study was conducted for nine months. The research demonstrated that for some periods aspirin concentration in the influent was negligible; for October – December the retention value of aspirin consisted 50 - 90.2%.

2. Materials and methods

2.1. Materials and reagents

Aspirin (pharmaceutical secondary standard) was purchased from Merck, USA. HPLC grade acetonitrile was obtained from Sigma Aldrich, USA. High pure water was obtained using Millipore Milli Q Integral 5 purification system, USA.

2.2 Sample collection and storage

Aqueous phase samples were collected before any treatment (1) and in the end of treatment process of Nur-Sultan wastewater treatment plant (2). The concentrations of target compound were measured using high-pressure liquid chromatography. Wastewater samples were taken from the initial influent and the treated wastewater effluent on the 20th of each month during morning peak flow hours. Samples were collected in 1 liter plastic bottles, screwed with a plastic cap and delivered to the laboratory. The analysis was carried out on the day of sampling

2.3 Sample extraction and analysis

For analysis, the samples were filtered through glass microfiber filters Whatman GF/F and glass fibre filters 0.2 μm Chromatofil CA 20/25.

2.4 HPLC measurements

UHPLC Ultimate 300 System (Thermo Scientific, USA) equipped with a isokratic detector (ID) was utilized in this study.

Currently, HPLC is a modern analytical method for the determination of drugs and their metabolites in various media [37-39]. An adapted HPLC method for aspirin determination was designed specifically for this research [18,22].Chromatographic separations were performed on a Hypersil Gold C8 column 150x2.1mm, with 1.9 μm particle size. The mobile phase-A contained ultrapure water – (45:55, v/v), and mobile phase-B contained acetonitrile. The flow rate was 0.3 mL/min and the detection was achieved at 238-280 nm. The injection volume was 100 μL with column oven at 25 °C (Table 1).

Table 1. HPLC method parameters for the detection of aspirin.

equipment	UHPLC Ultimate 300 System (Thermo Scientific, USA)

column	Hypersil Gold C8 column 150*2.1mm, with 1.9 µm particle size
column temp.	25 °C
mobile phase	45:55 water:acetonitrile
flow rate	0.3 mL/min
injection	100 µL
detector	UV, 238-280 nm

3. Results and Discussion

It was detected that aspirin was present in raw and treated wastewaters of Nur-Sultan wastewater treatment plant. Figure 1 shows the aspirin content in samples collected at the station between April and December 2021. Aspirin concentrations in raw wastewater ranged from 0.0028 mg/l to 0.0604 mg/l. The concentration in treated wastewater ranged from 0.0014 mg/l to 0.0065 mg/l.

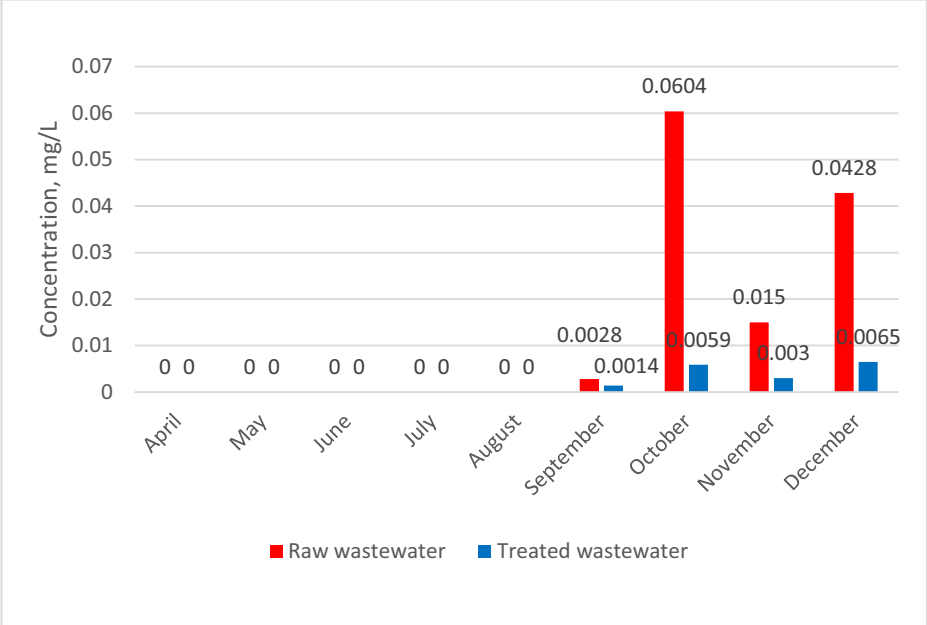

Figure 1. Concentrations of aspirin in influent and effluent to/from Nur-Sultan wastewater treatment plant.

Aspirin was found in samples of wastewater and treated wastewater, except for the spring-summer period of 2021. The results obtained were about several times higher than those reported by other published authors. Various authors indicated different concentrations of aspirin in wastewater using the different modifications HPLC method [30, 38-40]. For example, aspirin concentrations in samples from wastewater treatment plants in southwestern India, ranged from 0.4–0.7 µg/L [38], while in Japan it reached 7300 ng/L [39]. The total concentration of acetylsalicylic acid found in the sludge was 0.374-367.0 mg/kg [40]. The average concentration of aspirin in wastewater reported by [30[consisted 0.27 µg/mL.

As can be seen from Figure 1 influent concentration of aspirin changes from month to month. This

trend was observed by many authors and possible explanation is seasonal fluctuations in various medicinal substances in wastewater [41]. Seasonal fluctuations in the concentrations of aspirin in wastewater are most likely related to the nature of the diseases for which this medicine is used. This may be due to the use of aspirin for the treatment and prevention of seasonal flu in the autumn-winter period by the population of Nur-Sultan. From all mentioned above, it has been established that treatment facilities cannot completely eliminate all released drugs, but they can reduce their concentration. Table 2 below shows the dynamics of aspirin removal in wastewaters within studied period.

Table 2. Dynamics of aspirin removal in wastewaters.

Month	Removal, %
April	N/A
May	N/A
June	N/A
July	N/A
August	N/A
September	50
October	90.2
November	80
December	84.8

Based on the data obtained, the percentage of removal of aspirin varies. Overall, according to HPLC results, the removal of aspirin by wastewater treatment processes is between 50-90.2%. It should be noted that the maximum removal was observed in October and the minimal in September.It corresponds with influent concentration of aspirin, i.e. the highest and lowest concentration of aspirin in raw water was found for October and September, respectively. This finding is also under investigation by our research group at the moment.

4. Conclusions

Aqueous phase concentrations of an aspirin drug were determined in both raw and treated wastewaters from a municipal wastewater treatment plant in Nur-Sultan city, Kazakhstan. The study was implemented within nine months. The aspirin concentrations detected in this work were slightly greater than those reported by previous researches. The highest concentration of the aqueous phase of aspirin in raw wastewater was 60.4 ppb, and the concentration in treated effluent - 6.4 ppb. The resulting sample data showed that aspirin concentrations were substantially greater in the winter than in the summer.

The results demonstrate a continuous discharge of the drug into the wastewater treatment plant. There is no clear indication that aspirin is absolutely absent in wastewater in the spring-summer period, since most likely its concentrations are simply beyond the detection limits of the method. A population of more than a million people in a big city like Nur-Sultan is continually taking various medications, including aspirin. Because there are fewer cold-related diseases in the summer, it's likely that aspirin is taken in the smallest amounts. Increased use of pharmaceuticals, inefficient water and wastewater treatment systems, and inadequate disposal practices for expired and unused drugs can result in aspirin entering sewage treatment plants and further into rivers. According to the findings of this study, the general concentration of aspirin in treated wastewater is much lower than in raw wastewater. Currently our research team is working on investigation of other potential contaminants of emerging concern in municipal wastewaters of Nur-Sultan city and on treatment methods that could efficiently remove the contaminants of emerging concern.

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