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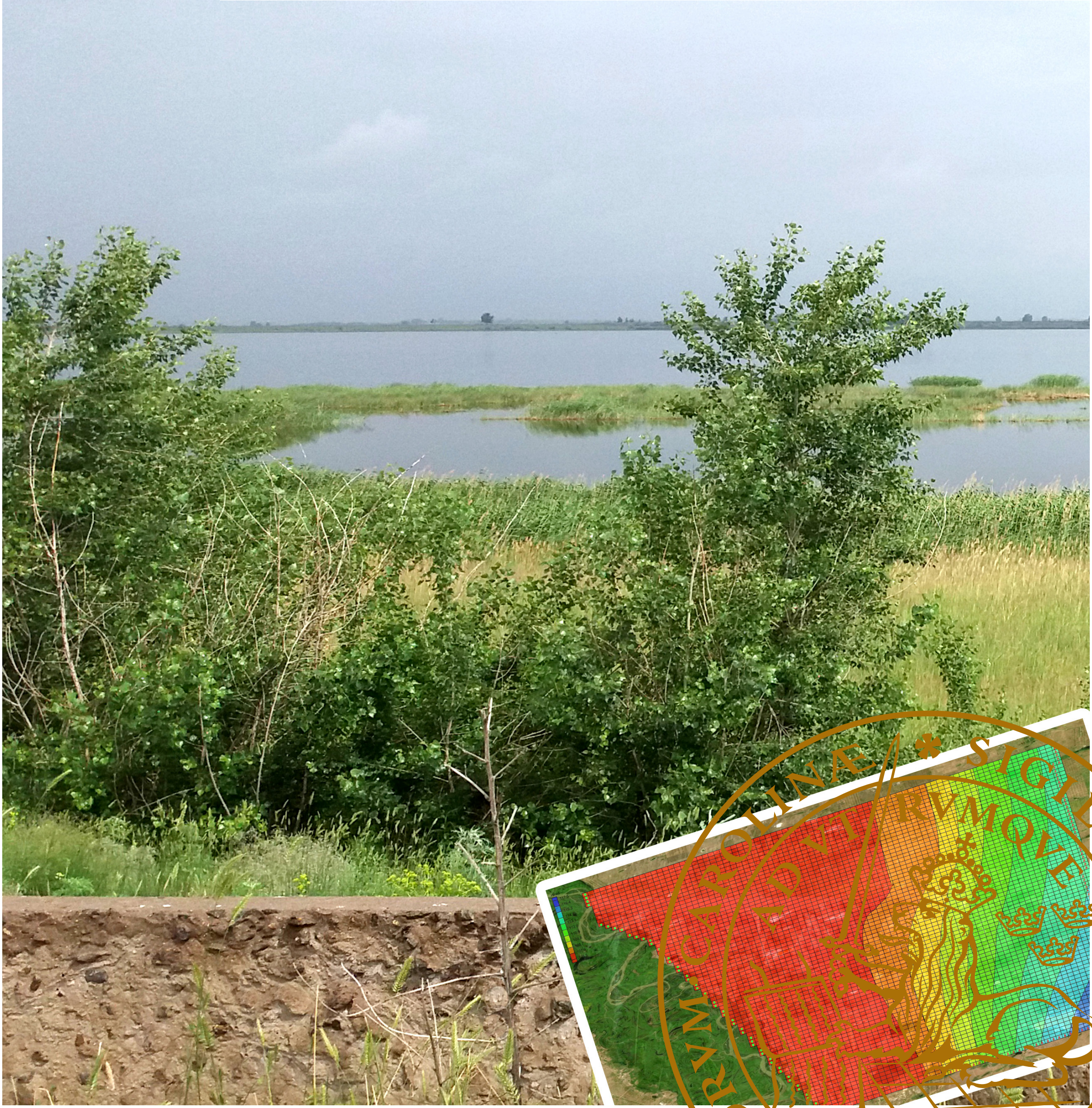

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Ivan Radelyuk

DOCTORAL DISSERTATION

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Abstract

The concept of “Sustainable water use” (SWU) aims to assure three pillars of sustainability related to the water sector: the social, environmental, and economical. Industrial development, especially in developing countries, requires an adequate response, as industrial activities are recognized as one of the major sources of water pollution, what leads to deterioration of environmental safety and wellbeing of the society. This thesis aims to understand to what extent the water use in the oil refinery industry in Kazakhstan is sustainable and to assess its impacts on the environment. A system approach was used to evaluate the current status of legislation, the treatment methods, the discharge process, and the effect on the environment in the sector. The weakness of the existing framework was identified by its lack of unified and transparent legislative standards for treatment processes, wastewater quality, and assessments of groundwater contamination with potential negative impact on public safety. Analysis of chemical characteristics of groundwater contamination, based on a seven-year monitoring program from one of the refineries, showed that groundwater has been affected, containing anthropogenically and naturally occurred contaminants, e.g. average exceedance for total petroleum hydrocarbons was 4 times, for total dissolved solids - 5 times, for chlorides - 9 times, for sodium - 6 times and total hardness was more than 6 times compared with World Health Organization and Kazakhstani standards. The analysis made it possible to specify the contribution of each contaminant to the overall pollution and to identify the most polluted sites. These pollutants are likely spreading towards areas with substantial groundwater use. The following investigation included performance of potential spreading of the TPH plume, based on historical observations. The results showed that zone at 2-6 km downstream the source of pollution could be affected by contaminated water, where concentrations of TPH exceeded permissible value. Based on performed investigations, this study highlights importance of implementation of suitable legislative standards with requirements for efficient water-saving techniques. Comparison with developed countries showed that Principles of Circular Economy (CE) (reduce pollution and reuse water) have been neglected in Kazakhstan. However, these principles have a potential to become a response to existing pressure of industrial activities and to achieve Sustainable Development as Driving force. Implementation of the CE for refineries in Kazakhstan requires firstly, the usage of advanced wastewater treatment techniques, and secondly, the introduction of the optimization scheme for water reuse, where regeneration units are established after each technological unit. Establishing criteria for water fees, wastewater quality, and recipients’ characteristics should follow respective and fair practices of the Environmental Impact Assessment, instead of looking for legislative loopholes. These practices include a detailed assessment of a real level of effluents’ toxicity and strict requirements to avoid the transfer of pollutants from one environmental media to another. Also, it is strongly recommended to update the list of contaminants for operational monitoring with inclusion of specific indicators of toxicity, such as PAHs, BTEX and others. It will let to understand the real harm caused by the ineffective systems of wastewater treatment and disposal from oil refineries in Kazakhstan.

This thesis can be used as a trigger to drive and engage all stakeholders into a transparent dialogue about potential consequences of non-sustainable wastewater management in the industry in Kazakhstan. The potential actions might include development of new efficient monitoring programs, stimulation the industry to innovative and water-saving treatment methods, and a creation of a site remediation program.

Key words industrial wastewater, oil refinery, Kazakhstan, groundwater contamination, groundwater modeling, contamination transport modeling, Sustainable water use, Environmental Impact Assessment, Circular Economy

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Dedicated to all staff, who works for kids with Autism Spectrum Disorder (ASD):
doctors, psychologists, psychiatrists, therapists,
teachers, tutors, nurses, scientists, et al.
To all parents, who struggle for the future of their kids with ASD

Посвящается всем тем, кто трудится для детей
с Расстройством Аутистического Спектра (РАС):
врачам, психологам, психиатрам, методистам,
терапистам, логопедам, тьюторам, исследователям, и др.
Всем родителям, которые сражаются за будущее их детей с РАС

Table of Contents

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And finally, to Almighty. For His Holiness, Sovereignty, and Grace.

Popular summary

Kazakhstan officially declares concern about environmental protection and promotes the "polluter pays" principle. Simultaneously, loopholes in the local law allow the discharge of improperly treated industrial wastewater into artificial or natural ponds, which potentially causes fate for environment and society. One example is that permission is based on the requirement that the initial concentration of pollutants in wastewater's recipient is exceeded. Historically, there has been a time gap between when the discharge started and when the monitoring of the recipient started. Thus, the industry receives a legal permit for environmental pollution and does not have any motivation to invest in the improvement of treatment techniques, or into modernization of already obsolete treatment equipment. Moreover, the situation is deteriorated by the facts that industry consumes a huge amount of water, the population is growing, and climate change leads to the reduction of available water resources. Hence, it is projected that the mismanagement of freshwater resources would lead to a national water deficit by 2030. There is only way to improve the situation - rational use of available resources, coupled with assurance of water safety via eliminating pollution. This concept is defined as "Sustainable water use".

This thesis investigates potential consequences of the current system of industrial water use in Kazakhstan based on an example of groundwater pollution, caused by the oil refinery industry. The most basic biological treatment method, activated sludge, which is used by refineries in Kazakhstan, cannot efficiently treat the industrial wastewater. Petroleum hydrocarbons are potentially toxic substances, which are practically ubiquitous in groundwater, usually low degradable, and may move over several km. Analysis of groundwater characteristics surrounding a recipient of effluents from the refinery showed that the groundwater quality has been affected by an unacceptable level of man-made contaminants, which are directly linked to refineries' activity. Rural residents of the studied area use groundwater from the shallow aquifer for drinking and domestic purposes. The current investigation considers the potentially affected sites where to avoid the consumption of unsafe water. The results show that, depending on initial loading, agricultural areas might be affected at a distance 2-6 km downstream the contaminated site.

The situation can be turned on 180 degrees if the pollution stops. Experience from developed countries shows that implementation of advanced wastewater treatment techniques ensures a good quality of the effluents. Moreover, the current trend is

one step ahead – to consider potential wastewater reused, such as alleviation of the stress on freshwater supply, recovery of resources, and elimination of environmental pollution. Also, the current Kazakhstani system of establishing requirements for maximum allowable concentrations of the pollutants in wastewater should be changed and based on the respective investigations of the toxicity of effluents. Specific potentially toxic contaminants are subjected to be controlled in the effluents to get a fair picture of the real harm for groundwater caused by oil refineries in Kazakhstan.

Strong political will is needed to translate concrete actions. This research presented in the thesis is important to show that "zero waste" approach for the industry in Kazakhstan is barely visible and the joint effect of governmental regulation, scientific approach, and industrial implementation can contribute to less impact and the precaution activities for Sustainable water use.

Abstract

The concept of “Sustainable water use” (SWU) aims to assure three pillars of sustainability related to the water sector: the social, environmental, and economical. Industrial development, especially in developing countries, requires an adequate response, as industrial activities are recognized as one of the major sources of water pollution, what leads to deterioration of environmental safety and wellbeing of the society. This thesis aims to understand to what extent the water use in the oil refinery industry in Kazakhstan is sustainable and to assess its impacts on the environment. A system approach was used to evaluate the current status of legislation, the treatment methods, the discharge process, and the effect on the environment in the sector. The weakness of the existing framework was identified by its lack of unified and transparent legislative standards for treatment processes, wastewater quality, and assessments of groundwater contamination with potential negative impact on public safety. Analysis of chemical characteristics of groundwater contamination, based on a seven-year monitoring program from one of the refineries, showed that groundwater has been affected, containing anthropogenically and naturally occurred contaminants, e.g. average exceedance for total petroleum hydrocarbons was 4 times, for total dissolved solids - 5 times, for chlorides - 9 times, for sodium - 6 times and total hardness was more than 6 times compared with World Health Organization and Kazakhstani standards. The analysis made it possible to specify the contribution of each contaminant to the overall pollution and to identify the most polluted sites. These pollutants are likely spreading towards areas with substantial groundwater use. The following investigation included performance of potential spreading of the TPH plume, based on historical observations. The results showed that zone at 2-6 km downstream the source of pollution could be affected by contaminated water, where concentrations of TPH exceeded permissible value. Based on performed investigations, this study highlights importance of implementation of suitable legislative standards with requirements for efficient water-saving techniques. Comparison with developed countries showed that Principles of Circular Economy (CE) (reduce pollution and reuse water) have been neglected in Kazakhstan. However, these principles have a potential to become a response to existing pressure of industrial activities and to achieve Sustainable Development as Driving force. Implementation of the CE for refineries in Kazakhstan requires firstly, the usage of advanced wastewater treatment techniques, and secondly, the introduction of the optimization scheme for water reuse, where regeneration units are established after each technological unit. Establishing criteria

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List of publications

Appended papers

I. **Radelyuk, I.,** Tussupova, K., Zhapargazinova, K., Yelubay, M. & Persson, M. (2019). Pitfalls of wastewater treatment in oil refinery enterprises in Kazakhstan—a system approach. *Sustainability* 11(6), 1618, https://doi.org/10.3390/su11061618

II. **Radelyuk, I.,** Tussupova, K., Persson, M., Zhapargazinova, K. & Yelubay, M. (2020). Assessment of groundwater safety surrounding contaminated water storage sites using multivariate statistical analysis and Heckman selection model: a case study of Kazakhstan. *Environmental Geochemistry and Health*, https://doi.org/10.1007/s10653-020-00685-1

III. **Radelyuk, I.,** Naseri-Rad, M., Hashemi, H., Persson, M., Berndtsson, R., Yelubay, M. & Tussupova, K. (2021). Assessing data-scarce contaminated groundwater sites surrounding petrochemical industries. *Environmental Earth Sciences* (accepted for publication)

IV. **Radelyuk, I.,** Tussupova, K., Klemeš, J.J. & Persson, K.M. (2021). Oil refinery and Water Pollution in the context of Sustainable Development: Developing and Developed Countries. *Journal of Cleaner Production*, https://doi.org/10.1016/j.jclepro.2021.126987

Author's contribution to the appended papers

The process of the research was based on collaborative principles via constant discussion of the methods and results with supervising and other co-authors.

I. The author together with supervising co-authors planned the whole study, and on his own collected and analyzed the data, produced initial results, and wrote the first draft of the paper. The other authors equally contributed by commenting on the first draft of the paper.

II. The author with other co-authors planned the idea of the research and on his own gathered data, performed the analysis, and wrote the first manuscript. Kamshat Tussupova conceptualized the idea of using the Heckman method. All authors commented on the first draft in an equal manner, helped with ongoing discussions and advice.

III. The author together with supervising co-authors planned the whole study, collected data, performed groundwater modeling, and analysed the initial results, and together with the second co-author wrote the first draft of the paper. Mehran Naseri-Rad conceptualized the idea of the semi-analytical contamination transport model and applied it together with the author. Co-authors contributed by discussing and editing the last version of the manuscript.

IV. The author conceptualized and performed the study, discussed the initial results, and wrote the first draft. Co-authors contributed by discussing, reviewing and editing the final version of the manuscript.

Other related publications

1. **Radelyuk I.,** Tussupova K. (2018). Assessing wastewater processes at oil refinery industry in Kazakhstan. In: SETAC Europe 28th Annual Meeting, Rome, Italy.
2. **Radelyuk, I.,** Tussupova, K. & Zhapargazinova, K. (2019). Assessment of groundwater safety around contaminated water storage sites. In: 11th World Congress on Water Resources and Environment [EWRA 2019], Madrid, Spain.
3. **Radelyuk, I.,** Tussupova, K. & Zhapargazinova, K. (2020). Impact of oily wastewater for public health in rural area: a case study of Kazakhstan. In: EGU General Assembly 2020, Online. https://doi.org/10.5194/egusphere-egu2020-11235
4. **Radelyuk, I.,** Tussupova, K. & Klemeš J.J. (2020). Oil refinery and Water Pollution in the context of Sustainability and Circular Economy. In: The 4th Sustainable Process Integration Laboratory (SPIL) Scientific Conference "Energy, Water, Emission & Waste in Industry and Cities", Brno, Czech Republic (Online).
5. **Radelyuk, I.,** Tussupova, K., Klemeš J.J. & Zhapargazinova, K. (2021). Sustainable Water use in Industry in Developing Countries – Reasons, Challenges, Response. In: 24th Conference on Process Integration for Energy Saving and Pollution Reduction - PRES'21, Brno, Czech Republic.

1 Introduction

The 2030 Agenda for Sustainable Development (SD) calls all people, from individuals to crucial stakeholders, such as governments, corporations, and international organisations to take actions for solving the current challenges, formulated in the Sustainable Development Goals (SDGs) (UN 2015). One of the common definitions of Sustainable Development is “Enhancing quality of life and thus allowing people to live in a healthy environment and improve social, economic and environmental conditions for present and future generations” (Ortiz et al. 2009). The concept of “Sustainable water use” (SWU) brings several SDGs, related to water, together. The SWU aims to assure three pillars of sustainability: social, environmental, and economical. Social aspects of the SWU include, firstly, public safety by consumption of available and safe drinking water, and secondly, relevant regulation. Environmental aspects of the SWU consider good ecological status of water bodies, where the water is supplied from and discharged to, including groundwater (GW). Economical aspects of the SWU include efficient and fair pricing for water use, which considers costs to obtain water, treat it and discharge or reuse it in a respective manner (USEPA 2012).

The SWU is a complicated system. It is clearly presented within related Sustainable Development Goals (SDGs). When one of the elements does not work, it affects the success of the other goals and crashes the whole system of SD (Figure 1). The group of SDGs 8, 9, 12, and 13 belongs to the sustainable industry. This group is directly connected with the industrial processes related to water use. The processes should be innovative to achieve rational and efficient resource use (SDGs 8, 9, 12) and eliminate impact on the environment through sufficient treatment systems, which lead to the deceleration of climate change (SDG 13). The SDG 6 “Clean Water and Sanitation” requires, firstly, eliminate potential hazards of inappropriately treated wastewater; secondly, to adopt water-saving techniques to reduce the consumption of fresh water to address water scarcity (Jia et al. 2020); and, thirdly, protect water-related ecosystems, including rivers, lakes and aquifers. The SDG 14 “Life below Water” specifically focuses on the consequences of any kind of pollution for the aquatic world. Healthy environment (water, soil and air) is directly linked with the quality of life of people, which belongs to SDGs 3 and 11.

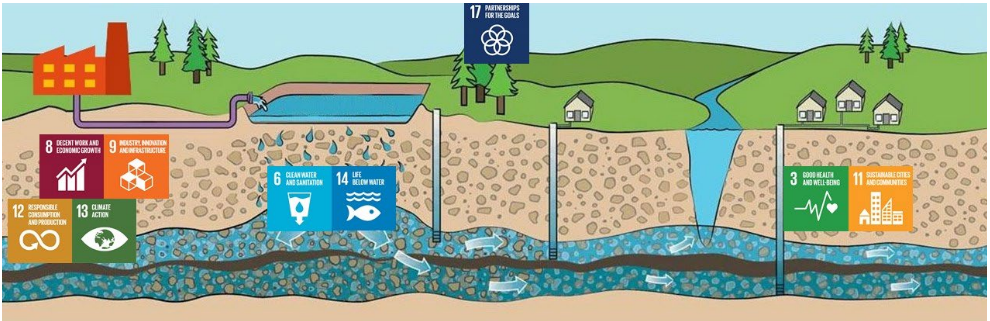


Figure 1 The interactions between SDGs related to the SWU (Paper IV)

Industrial activities are recognized as one of the major source of pollution worldwide (Hossain 2011). Fast industrial development, aiming economic growth, however, puts pressure on environment, which in turn may jeopardize wellbeing of society (Li 2016). Currently, water consumption by industry ranges between 10% and 57% of total water consumption in different countries (Voulvoulis 2018). This range mainly depends on the efficiency of collaboration between key stakeholders: under governmental regulation via implementation of water-saving technologies by the industry with the support of research-based decisions.

According a UN "World Economic Situation and Prospects 2019" book, Kazakhstan has been rated as a fuel-exporting country with transitional from developing to developed economy (UN 2019). This type of country is characterized by applying efforts to diversify the economy from just exporting resources to build advanced technological infrastructure. This process includes accelerated industrialization and growth of an already existing manufacturing capacity. Although, Kazakhstan shows an increasing trend of gross national income per captia for the processing industry, a changing world requests new challenges and adaptation rules for society. The productive economy should not only meet monetary benefits; safe environment and social issues must also be brought to the forefront.

The refining enterprises also give a significant contribution to the structure of industrial development (Kazakhstan 2009). Kazakhstan is the second biggest oil producer after Russia among the Commonwealth of Independent States countries. The petroleum industry is the major actor and accounted for about 10% of the country's GDP in 2016 (KASE 2017). Kazakhstan is one of the key suppliers of hydrocarbon raw materials for the world economy. In 2016, Kazakhstan was rated number 16 in the world with a production volume of 79.3 million tons of oil and gas condensate (representing 2% of the global production). The refinery throughput in Kazakhstan is 339 thousand barrels daily, a number that is growing by 4.6% every year. The refinery capacity is estimated to be 350 thousand barrels daily (BP 2019).

Water is a very important reagent in petroleum and petrochemical production processes. Distillation, extraction, preparation of solutions, cooling systems, and washing processes are some examples of industrial water use, leading to large consumption in the current fuel and electricity production (Walker et al. 2013). The total water consumption for those purposes is projected to increase by 55% between 2000 and 2055 globally (Wangt and Zimmerman 2016).

The problem of the water use in the industry is twofold: huge amounts of water are consumed, while the quality of the wastewater is poor and does not satisfy the principles of the SWU. Up to 65% of all fresh water in Kazakhstan are lost due to wasteful and polluting activities. Simultaneously, the industry consumes about 25% of all available freshwater in Kazakhstan (Karatayev et al. 2017). This would lead to a national water deficit by 2030 (Thomas 2015). The oil refinery industry in Kazakhstan consumed 77.8 mln m^3 water in 2016, while only 3.5 mln m^3 of it has been re-used, the rest has been discharged into the environment. According the Environmental Performance Review for Kazakhstan (UNECE 2019), three oil refinery factories in Kazakhstan are one of the biggest sources of water contamination, despite attempts to control the pollution by both the government and the industry. This thesis is the first attempt to investigate the industrial water management system in Kazakhstan from the perspective of the SWU concept on the example of the oil refinery sector.

1.1 Thesis objectives

Sustainable water use in the industrial context covers several factors of three dimensions of SD and their interactions, as shown in Figure 2. Economic factors are represented by the processes inside the industry. The industry uses technologies to treat supplied and processed water, and to utilize it in a safe manner. These technologies are associated with respective costs. Environmental factors consider water quality in water sources and wastewater recipients. Interactions between economical and environmental factors are characterized by attempts to decrease the impact of industrial activities on water bodies and make water viable for other consumers by the use of efficient treatment technologies. Social factors are represented by ensuring public safety (e.g., health), and are mainly regulated by government. The government assures the availability of safe water by respective legislative and environmental tools. Economical and social factors are met by establishing the idea of equal rights of different water users. Thus, appropriate legislation ensures responsibility of the industry to apply respective efficient and water-saving technologies.

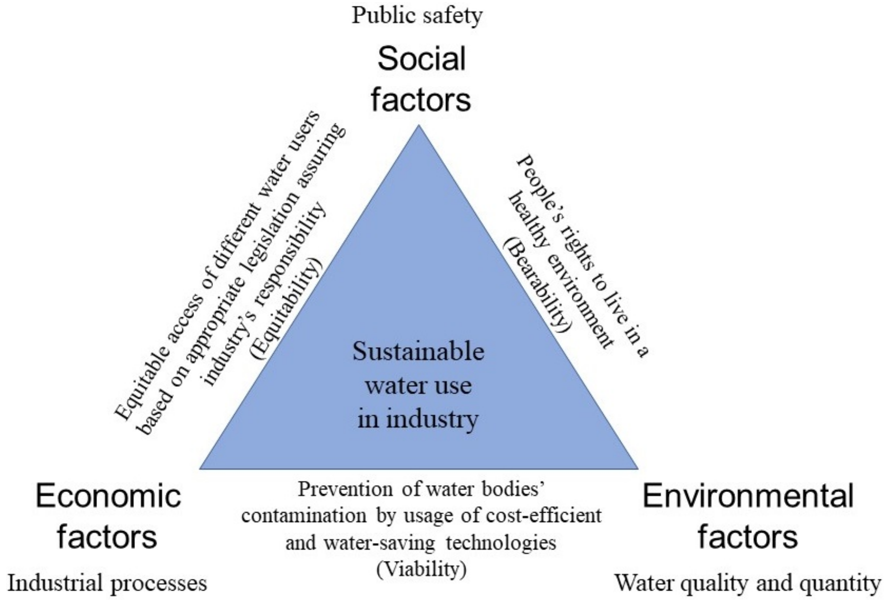


Figure 2 The Sustainable water use in industry framework used in the thesis

The general aim of this work was to understand, to what extent the water use in the oil refinery industry in Kazakhstan is sustainable and to assess its impacts on the environment. Respectively, three objectives related to interactions between dimensions of the SWU were identified for related investigation:

Objective A was aimed to investigate water and wastewater management at oil refinery factories in Kazakhstan in accordance with respective national and international legislation. This objective is mainly addressed in **Paper I**, and covers the efficiency of implementation of Kazakhstani regulation and practices of the refineries of water use, treatment, and discharge, using a system approach.

Objective B was aimed to assess groundwater safety affected by the current system of wastewater treatment in refineries. Statistical tools were used in **Paper II** to assess the contribution of each contaminant, both natural and man-made. **Paper III** evaluates the effect of pollution by developing respective groundwater and contamination transport models.

Objective C was aimed to define possible solutions for industrial water and wastewater management system in Kazakhstan to ensure the SWU. This objective is mainly presented by **Paper IV** that offers available mechanisms to achieve the SWU. **Paper III** highlights a possibility for usage of analytical modeling tools for better governmental regulation of industrial waste management with limited data availability. Also, **Paper I** discuss the importance of suitable regulative standards for improvement of industrial water use management.

2 Methodology

2.1 Study area

2.1.1 Oil refinery sector

2.1.1.1 Technological processes

Modern refineries are sophisticated complexes for separating and modifying crude oil into different products. The general scheme of it is presented in Figure 3. The main objective of the refineries is production of fuel, residual fuel oils, lubricants and many other petrochemical and chemical products. The initial refinery configuration was the topping refinery, which was designed to distil crude oil into a limited range and yield of products. It was composed of different units such as tankage, atmospheric and vacuum distillation units, recovery facilities for gases and light hydrocarbons, and the necessary utility systems such as steam, power, and water-treatment plants. The addition of hydrotreating and reforming units to this basic configuration resulted in a more efficient hydroskimming refinery, which produced desulfurized distillate fuels and high-octane gasoline. At the same time, refineries processed up to half of incoming crude oil. During the last 30 years, refinery complexes have been modernized. Initially, a gas–oil conversion plant and a catalytic cracking unit were added. In the last five years, an olefin conversion plant, a polymerization unit and coke calcination units were implemented in the existing scheme of plants. The changes allow enterprises to increase processing depth and thereby produce large outputs of gasoline with the remainder of their products distributed among liquefied petroleum gas, jet fuel, diesel fuel, and a small quantity of coke. Additionally, refineries also supply different substances, such as propylene, benzene, toluene, xylenes, etc., for further processing into polymers (Kent et al. 2017).

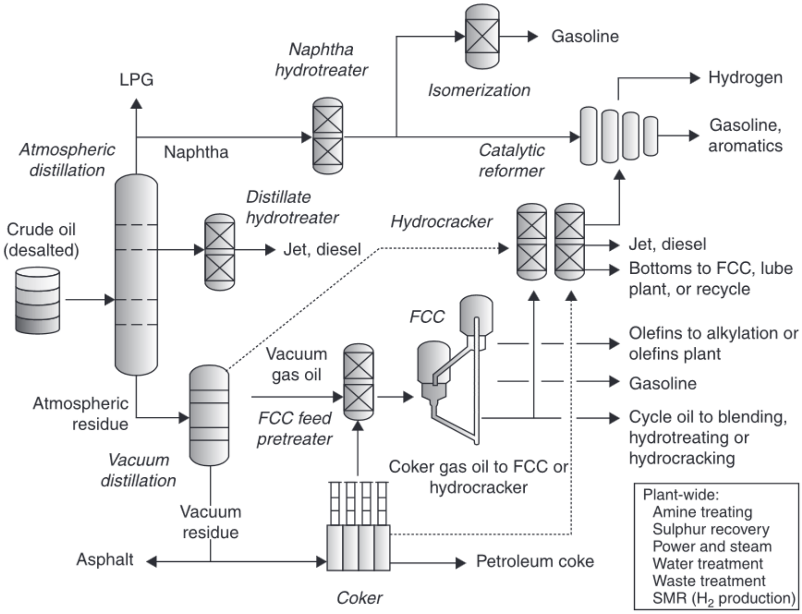


Figure 3 General scheme of an oil refinery plant (P.R.Robinson 2011)

2.1.1.2 Water use and sources of pollution inside the factory

The oil refining process starts in the atmospheric and vacuum distillation units. Those units are associated with the consumption of a number of by-products and reagents, including water, which is used for various purposes. For instance, as a cooler of process units and equipment, and a cooling agent of the final product. Water is also used as a solvent for the preparation of reagent solutions as well as a source of steam or condensate. Furthermore, other reagents are added during a technological process, such as demulsifiers for dehydration of oil, ammonia to neutralize organic acids and sulphur compounds for purification of light distillates.

There are three main sources of wastewater contamination at the refinery. Firstly, recycling of sulphurous oil and purification of petroleum products with alkalis, which gives highly concentrated sulphurous alkaline wastewater. Secondly, complex processing of oil and gas to produce synthetic products generates wastewater with organic acids, alcohols, phenols, etc. Thirdly, processes of desalination and dehydration. In the final source, wastewater contains demulsifiers and sulphonaphthones. All these substances are sources of harmful chemicals, which lead to environmental pollution (Yu et al. 2017).

It is necessary to emphasize the harmfulness of some chemicals. Oily wastewater consists of hundreds of organic and non-organic compounds, some of them may severely jeopardize the environment. Effluents include aromatic hydrocarbons which have high toxicity and have a stable structure. One of those are polycyclic aromatic hydrocarbons (PAH), which are characterized as persistent and have carcinogenic, teratogenic and mutagenic properties (Alegbeleye et al. 2017). Other group of hydrocarbons in contaminated water is BTEX (benzene, toluene, ethylbenzene and xylenes). High concentration of those compounds can be rapidly absorbed by the human body. They can lead to damage of the brain and nervous system, rapid heart rate, dizziness and unconsciousness (Leusch and Bartkow 2010). Phenols are considered very hazardous for human health (Huang 2007). Potentially toxic metals like chromium, iron, nickel, copper, molybdenum, selenium, vanadium and zinc can also be found in wastewater from oil refineries (Wake 2005).

2.1.1.3 Treatment methods

Conventional purification schemes for oil refineries include a broad variation for each step of treatment: pre-treatment, primary, tertiary (secondary) and post-treatment (or polishing). Figure 4 presents a general scheme of a wastewater treatment unit with the list of commonly used techniques for each step, which aim to enhance the efficiency of contaminants removal. The specific method chosen for any individual case will depend on the content of the pollution and local characteristics.

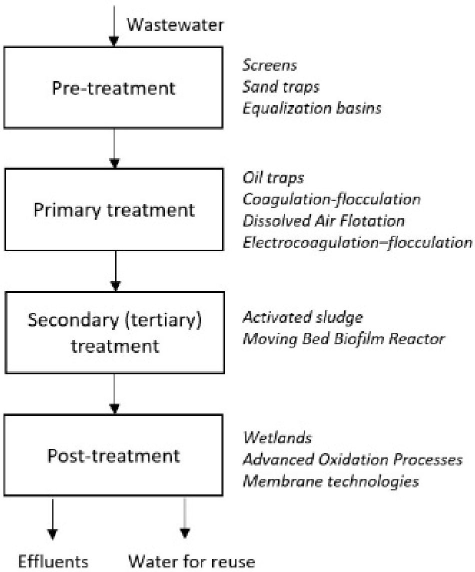


Figure 4 General scheme of wastewater treatment processes at oil refineries (Paper I)

2.1.2 Case study description

2.1.2.1 Treatment and Utilization strategy in Kazakhstani refineries

All factories in Kazakhstan use the same wastewater treatment system, consisting of an on-site mechanical (as a primary step) and a biological (as a secondary step) treatment. The biological treatment facilities of the refineries were built during the Soviet Union period, and are in need for modernized. They include a basic system of activated sludge treatment, which is not adapted for an efficient removal of heavily degradable fractions of petroleum hydrocarbons. The technology of wastewater treatment at the studied refinery is presented as an example of the same work of treatment facilities in all Kazakhstani refinery plants in Figure 5.

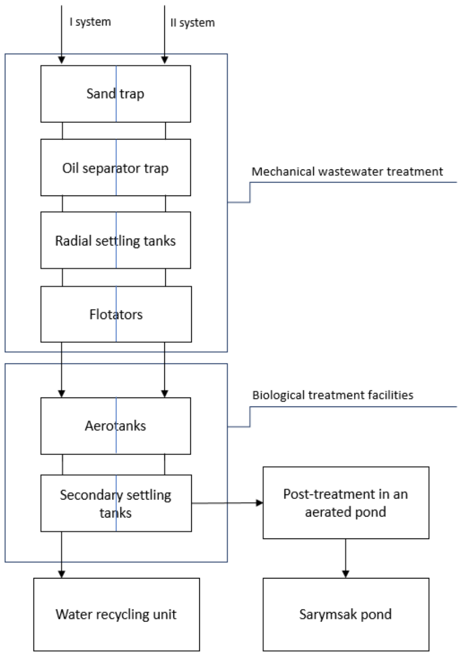


Figure 5 The block diagram of wastewater treatment processes at the studied refinery (Paper I)

The studied refinery uses a pipeline to deliver effluents to the special recipient pond. The pond is located 14 km to the north-west from the plant and covers the area of 606.1 hectares. The pond is originally a natural bitter-salty pond that now is used for receiving and storing biologically treated wastewater from the nearby located petrochemical industry. According to Kazakhstani legislation (Kazakhstan 2012), this pond is not a source for drinking, domestic and irrigation water. The annual volume of received wastewater amounted to 1.63-2.21 million m^3 for the period 2009-2019, instead of designed 4.12 million m^3. The water volume and water

surface for the same period are maintained within 3.6-6.7 million m^3 and 2.45-3.73 km^2, respectively, instead of the designed 23.5 million m^3 and 5.23 km^2, respectively.
Observation wells are located outside the barrier for groundwater quality monitoring. The wells belong to a permanent control from governmental bodies. The concentration of contaminants should not exceed the permissible limit for drinking water at the boundary of a sanitary zone (1000 m from the source) (Kazakhstan 2015). The installation procedures followed appropriate installation techniques in case of required installation materials and methods and planning of the location of the monitoring system (Houlihan and Lucia 1999). The depth of the wells varies between 10.1 and 24.6 m below ground level. The groundwater table in the wells varied between 1.1 and 4.9 m below ground level. There are two villages around the pond: Berezovka village 2.5 kilometers to the north and Michurino village 8 km to the north-west. The main water source in Kazakhstan, Irtysh River is located 9 km west of the pond. Agricultural fields with potatoes and carrots are also located nearby, where irrigation water is supplied from shallow groundwater.

2.1.2.2 Geographical and hydrogeological area characteristics

The Pavlodar region is one of the largest industrial centres in Kazakhstan. Metallurgical, chemical, and petrochemical cluster activities deteriorate the environmental situation of the region. The local petrochemical cluster is a major actor in the industrial activities and the main taxpayer in the region, which contributes for about 50% of the city budget (Neftepererabotchik 2019). The residents of the rural area near the industrial zone use the groundwater from the shallow aquifer for their drinking and domestic purposes (Tussupova et al. 2016). Hydrocarbons, originated by the petrochemical industry, are practically ubiquitous in groundwater, usually low degradable, and the plume scale might be spread out to km scale (Balderacchi et al. 2013).

The industrial site of this study belongs to the special economic zone and is located in the north-eastern part of Kazakhstan (Figure 6). The region is located in the continental zone, where mean monthly temperatures range from -19.3˚C in January to +21.5˚C in July, with an annual mean of 3.5˚C, absolute maximum of +42˚C and absolute minimum of -47˚C. Annual precipitation is around 303-352 mm, including 264 mm in liquid phase. The driest months are May, June and July. Annual evaporation is reported around 957 mm (Heaven et al. 2007). Average relative humidity equals 82% and 45% for the coldest and the hottest period of the year, respectively. Around 70-85 days of the year have a relative humidity of 80% or more.

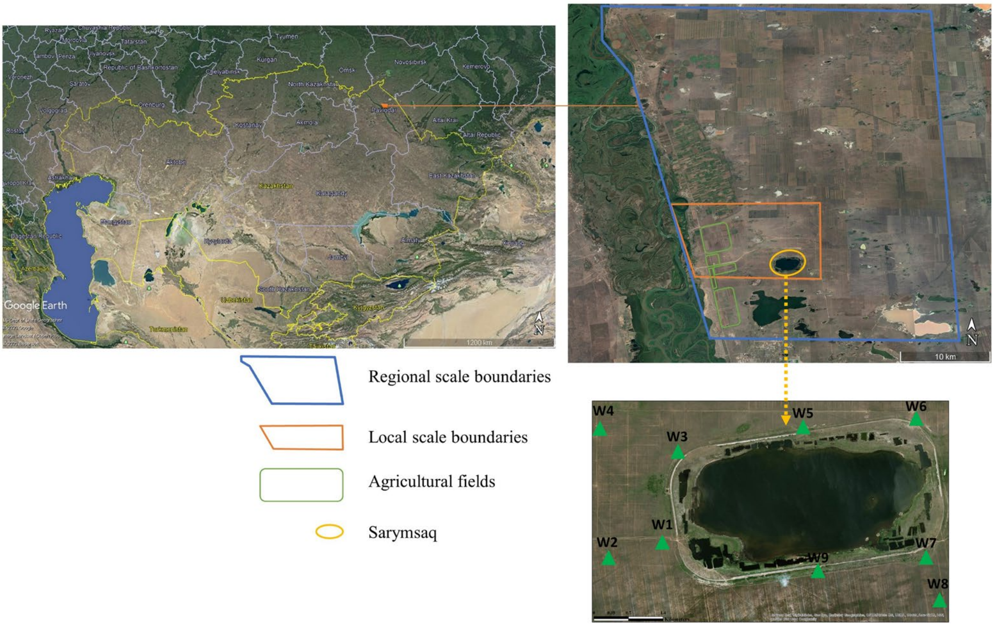


Figure 6 Study Area. Green triangles show location of wells sampled

The hydrogeological cross-section is mainly represented by three formations. The formation of Upper-Quaternary deposits of the first supra flood plain terrace (aQ_{III}), which is distributed along Irtysh River, 4-5 km wide. The water-bearing sediments consist of quartz-feldspar sands. The top layer is composed of sandy loam and loam, the bottom layer is composed of gravel and pebbles. The thickness of the formation is up to 20 m. The groundwater in the aquifer has a free surface (unconfined). The aquifer complex in Upper-Miocene Lower-Middle-Pliocene deposits of the Pavlodar suite ($N_{1-2}pv$) is distributed over the entire region. The thickness varies from 2-7 m in the northern and northwestern parts of the study area, and increase in a southeasterly direction to 80 m. These sediments are characterized by uneven distribution and the occurrence of sand among the clays. Water-bearing sediments in these aquifers consist of quartz-feldspar and micaceous sands. The sands are coarse-grained with gravel and pebbles in the south, and a fine-grained, sometimes clayey texture, in the north. Groundwater is mostly confined and occurs at a depth of 2-28 m to the surface. The formation of the Kulunda formation (N_2kln) is partly included in the Pavlodar formation. The thickness varies between 5 and 26 m. The water-bearing layer is characterized by alluvial sand, mixed with gravel and pebbles, with clayey and loamy lenses. The Pavlodar formation covers the Tavolzhan formation (N_1tv). This layer (N_1tv) consists mostly of clay that constitutes a bottom for the upper formation. The lithology of the area is presented in Figure 7.

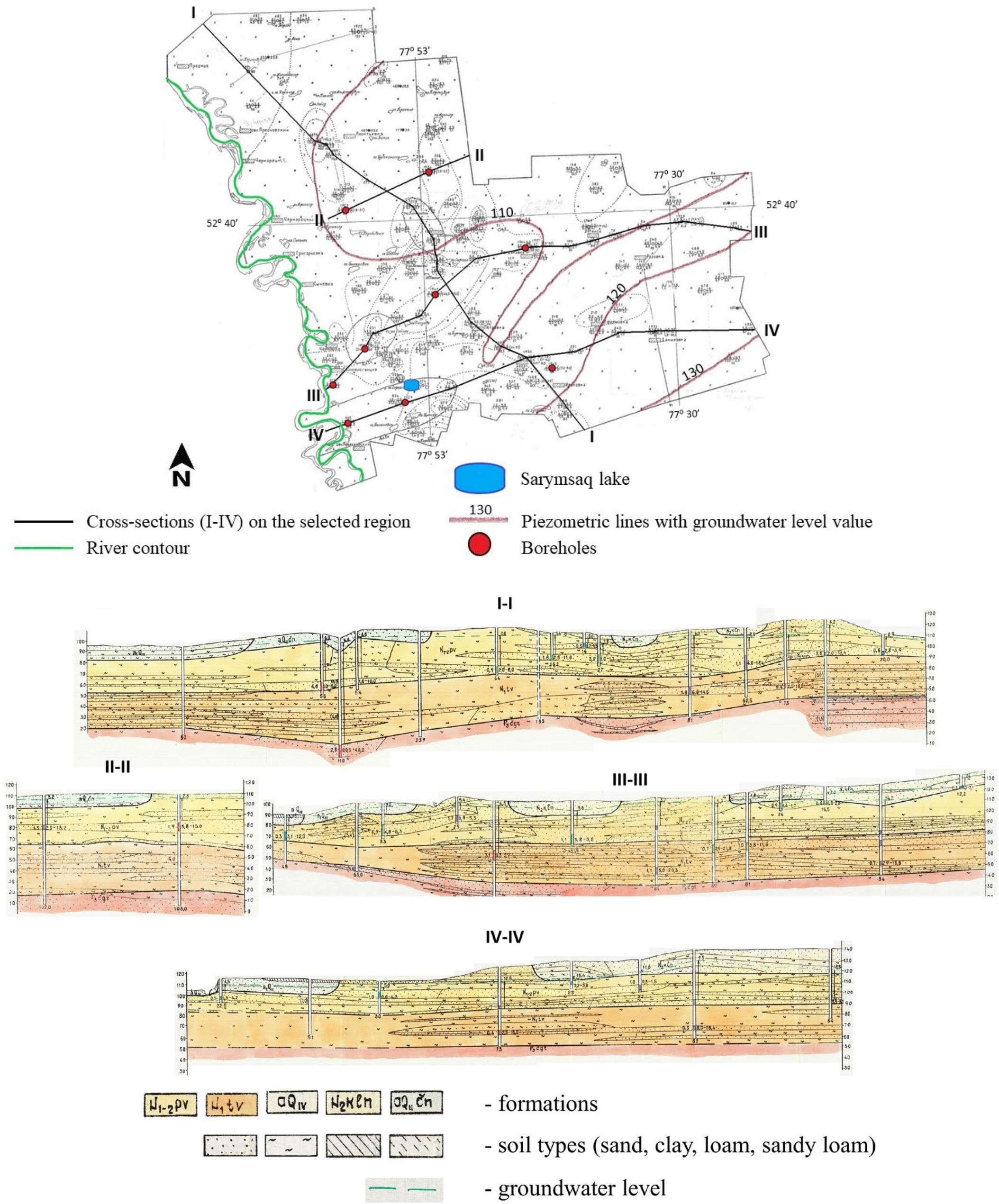


Figure 7 The lithology of the study area

2.2 Methods applied

2.2.1 Policy and literature review (Paper I and IV)

Principles of Environmental Impact Assessment (UNEP 2019) were used for investigation the potential effects of the existing scheme of industrial water use in the oil refinery sector in Kazakhstan to provide information about adverse impact on environment and people health.

The present study implemented the DPSIR (Drivers-Pressures-State-Impact-Response) framework (EU 2002) for the respective search, as is shown in Figure 8. Nowadays, principles of the SWU have become the *drivers* to meet socio-environmental awareness; and to decrease the *pressur*e on water resources. The hypothesis is that the *pressure* is caused by improper wastewater treatment. The resulting *state* (as an indicator of the *pressure*) is used to evaluate potential *impact*, which may differ, including deteriorated or destroyed ecosystems, unsafe drinking water, or the waste of water in the regions, where the water scarcity exists. The related *response* aims to improve the situation.

As a starting point, available “first-hand” information from governmental and representative bodies about the current status of water use in the oil refinery sector was analyzed. The sources of information included Kazakhstani legislative documents, such as laws, orders, reports, guidelines, and standards; documents, and reports from responsible authorities, such as Environmental Protection Agencies and oil refinery operators, and statistical datasets. The same sources from WHO, EU, and USA were compared with Kazakhstani analogues. The criteria for consideration of the information as relevant were 1) existing effluents conditions, including a description of the contaminants and their concentrations and 2) description of ways of effluent disposal and characteristics of wastewater recipients. Together with the analysis of official information, an extended literature review was carried out. The above criteria were used for consideration of the relevance of the reviewed literature as well.

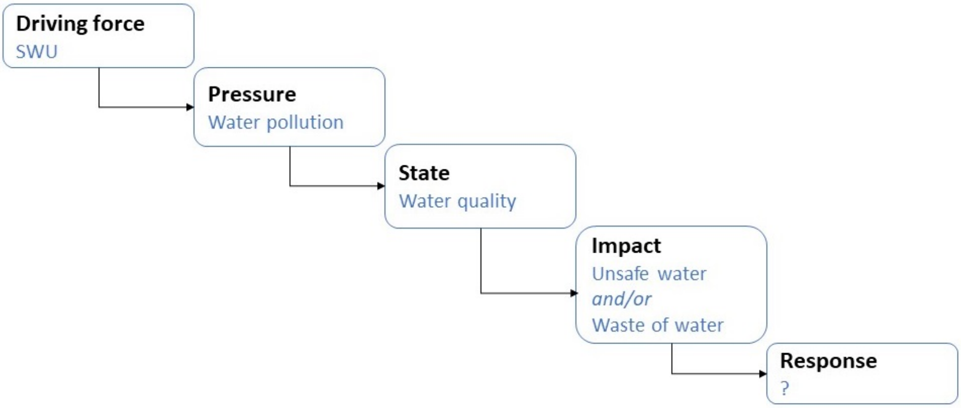


Figure 8 The DPSIR framework for this study

2.2.2 Data preparation (Papers I-III)

Data needed for empirical investigations have been collected from personal communication with representatives from the refineries and governmental offices. The dataset from the monitoring program consisted of a total of 117 groundwater samples from observation wells in the shallow aquifer near the recipient, collected and analyzed between 2013 and 2019. Sampling was made two times per year, in spring and autumn. The groundwater depth was measured regularly from March to November each year. The procedures of the sampling and measurements are controlled by Kazakhstani legislation and were adapted from international standards. Before sampling, the groundwater in the well was evacuated several times (at least three times) by pumping. The pumping equipment was also flushed before sampling to avoid unwanted pollution. After establishing a static water level, the sampler was immersed to a depth below the water table by 0.5 m or less. Water samples were collected in one-liter dark glass bottles. The vessels were placed into a transportable fridge for immediate delivery and analysis to the licensed factory laboratory. Extra samples were collected for the analysis of metals with acidification by HNO_3.

The investigations of the hydrogeological conditions, used for contamination transport modeling, have been conducted during the Soviet and post-Soviet periods (Kosolapov et al. 1993). Several recent available field surveys confirm the information from the previous investigations, which provides quality assurance of the data.

2.2.3 Multivariate statistical analysis (Paper II)

Correlation analysis, principal components analysis (factor analysis), and hierarchical cluster analysis were applied to identify the multivariate relationships between different chemical variables and samples in groundwater belonged to the study area. The dataset was normalized for elimination of the effect from differences in units.

The relation between each pair of variables was measured by Pearson's correlation coefficient to determine the geochemical associations among different variables. Correlation coefficients greater than 0.5 were considered significant. PCA recognizes the most significant parameters from a big dataset of inter-correlated parameters and created independent variables (Eqn. 1).

$$z_{ij} = a_{i1}x_{1j} + a_{i2}x_{2j} + \cdots + a_{im}x_{mj} \qquad (1)$$

where z is the component score, a is the component loading, x is the measured value of variable, i is the component number, j is the sample number and m is the total number of variables.

Cluster analysis was used to assemble similar groups of observed wells due to similarities between their variables. Hierarchical agglomerative CA provided Ward's linkage distance, reported as D_{link}/D_{max}, which represents the quotient between the linkage distances for each case divided by maximal linkage distance. Produced dendrogram enables analysis of similarities in an easy way. Ward's linkage, the Euclidean distance as similarity measurements and Q-mode were used for cluster analysis for assessment of groundwater quality.

2.2.4 Heckman selection model (Paper II)

The Heckman selection model was adapted from the original work of Heckman in the economical science (Heckman 1979) and from the application of this method in other fields. The method in this thesis was used to assess unobservable variables, that potentially impact on the total contamination rate. The idea of this assessment was not just to look at several contaminants and their concentrations, but also to consider and evaluate impact of other important factors such as location of the sample, percent of exceeding of the target values of each contaminant and individual characteristics of the contaminant. Selected variables were divided into two categories. First: chemicals seriously affecting health (rated as sanitary-toxic due to Kazakhstani standard (Kazakhstan 2015)); second: other hazardous materials (rated as non-toxic). It was aimed to compare potential effect of contaminants with high and low level of toxicity (or toxic and non-toxic contaminants in the following text). The focus was, on the one hand, on several pollutants with elevated concentrations, such as chlorides or sulphates, which are not rated as significant impact on health, but can be dangerous for other cases, for instance, for corrosion of pipes, or for irrigation properties of soil; on the other hand, on the contaminants, rated as dangerous for the health, or toxic (for example, hardness or petroleum hydrocarbons).

This model includes two-step equation, which is assumed as a regression model equation:

$$Y_i = \beta_1 S_i + \beta_2 X_i + u_i \qquad (2)$$

where Y_i is considered as total contamination, S_i represents the concentration of chemicals, and X_i shows several contaminants as a set of control variables. The effect of the exceeded concentrations on the total contamination is given by the parameter β_1. Parameter i represents each individual observation.

Eqn. 2 does not consider other potentially important independent variables which can affect final result. For example, it could be location of the well or individual characteristics of different contaminants such as their toxicity and exposure level in case of influence of chemicals for people's health. There could be a different input of high exceeding of non-toxic contaminant and low exceeding of toxic contaminant. The latter would be much more dangerous for health. Thus, more attention should be paid to the level of toxicity. To consider that, Eqn. 2 can be specifically re-written as:

$$\begin{aligned} Y_i^* &= \beta_1 S_i + \beta_2 X_i + u_i \\ D_i &= 1(\gamma_1 S_i + \gamma_2 Z_i + \nu_i > 0) \\ Y_i &= Y_i^* D_i \end{aligned} \qquad (3)$$

where (Y_i, D_i, S_i, X_i, Z_i) are observed random variables and 1(.) is an indicator function. The first equation represents the total contamination of all contaminants. The second equation is the selection equation, where D_i is added as a dummy variable indicating whether value i represents a measurement of toxic/non-toxic pollutant. A set of variables Z_i includes additional parameter such as a well value i. Set of control variables Z_i must include at least one variable which is not included in X_i (Sartori 2003).

In the studied case, the first dependent variable (D_i) represents toxicity of the chosen parameter (1 if the pollutant is toxic and 0 if not). The second set of dependent variables (Y_i) includes percentage of exceeding. This characteristic mathematically represents the rate of contamination. Mean percentage of selected (toxic or non-toxic) exceeding was calculated. For example, TPH has a standard value of 0.1 mg/L, if the measure concentration of TPH was 0.25 mg/L, then the dependent variable equals 250%. This variable includes only exceeded values, if the value is below the permissible limit, the cell in the matrix is empty. Set of control variables

(X_i) includes chosen contaminants, their concentrations, and locations. Thus, Eqn. 2 and Eqn. 3 were adapted as:

$$\% \text{ of exceeding} = \beta_1\text{chemical} + \beta_2\text{concentration} + u_i \quad (4)$$

and we assumed that "% of exceeding" is estimated if

$$\gamma_1\text{toxicity} + \gamma_2\text{number of well} + \gamma_3\text{chemical} + \gamma_4\text{concentration} + \nu_i > 0 \quad (5)$$

where u_i and ν_i should have positive correlation ρ.

2.2.5 Environmental fate assessment (Paper III)

The method proposed in this thesis aimed to evaluate the risks, by firstly: identification of the potentially affected territories by the spreading of the contamination plume in space, based on historical observations; and secondly: to assess the potential hazard from spreading of the contamination under potential scenarios of varying loading of the contaminants. For this purpose, a two-step procedure was used. The first step included the numerical groundwater model using MODFLOW to define the groundwater flow direction, as it is a necessary prerequisite to any contaminant transport modelling undertaken as part of the analysis of the pollution *pressures* on that body (EU 2002). In the second step, a semi-analytical contamination transport model was applied for general investigation of plume development in the aquifer. As a result, the potential fate of contaminants can be assessed under consideration of different scenarios, depending on local conditions.

2.2.5.1 GW modeling

A conceptual model is an efficient tool for simple presentation and understanding of transport processes (Todd and Mays 2005). One of the most popular and efficient models is MODFLOW-2000, which has been developed by McDonald and Harbaugh (Harbaugh et al. 2000). The principal equation is based on the three-dimensional groundwater flow equation for porous medium using a finite-difference method. The Groundwater Modeling System (GMS 9.0) software was used to perform the modelling at steady-state condition (Eqn. 6).

$$\frac{\partial}{\partial x}\left(K_{xx}\frac{\partial h}{\partial x}\right) + \frac{\partial}{\partial y}\left(K_{yy}\frac{\partial h}{\partial y}\right) + \frac{\partial}{\partial z}\left(K_{zz}\frac{\partial h}{\partial z}\right) \pm W = 0 \quad (6)$$

Where K_{xx}, K_{yy}, and K_{zz} are hydraulic conductivities along the x, y, and z coordinates assumed to parallel to the major axes of hydraulic conductivity (L/T); h is the potentiometric head (L); and W is a volumetric flux per unit volume, representing sources and/or sinks of water. Steady state modeling is the optimal option to calibrate the boundary condition as well as simulating the general GW flow. Thus, the steady-state conditions were assumed for the model, as the best option under data unavailability, such as lack of information about temporal changes of groundwater level, recharge, and discharge rates.

The PEST package (Doherty et al. 1994) was used to calibrate the results of the modeling by minimizing the difference between simulated and observed groundwater levels, as those measurements were available and chosen as the core of the calibration processes. The values for hydraulic conductivity, conductance, and drainage were assigned with ranges based on reported data. The process of calibration is considered successful when the root mean squared error (RMSE) residual of head is less than a certain value relevant for local conditions (1 m, as default) (Fienen et al. 2013).

When GW modeling and calibration was done, a tool of particle-tracking for MODFLOW, MODPATH, was used to assign the required coordinates for contamination transport modeling via displaying the groundwater patterns in a study area (Pollock 2012).

2.2.5.2 Analytical contamination and fate transport modeling

The transport model incorporates a steady-state solution for groundwater flow as a starting point to compute how concentrations of dissolved contaminants from a plan source change over time as they are transported in groundwater by advection and dispersion. This accounts for the role of varying hydraulic conductivity and other spatially variable hydraulic parameters that accompany aquifer heterogeneity. The transport model used for this purpose is based on partial differential equations for dispersion that have been developed for homogeneous and isotropic media, where Darcy's law is valid (Bear 2013).

According to Sauty (Sauty 1980), if a tracer is continuously injected into a uniform flow field from a point source, contamination will spread as it is shown in Figure 9. In this case, flow is governed by Eqn. 7, where mass transport can be calculated in two dimensions:

$$\frac{\partial C}{\partial t} = D_L \frac{\partial^2 C}{\partial x^2} + D_T \frac{\partial^2 C}{\partial y^2} - v_x \frac{\partial C}{\partial x} \qquad (7)$$

where v_x is down gradient fluid velocity, D_L is longitudinal dispersion coefficient (L^2/T), D_T is transverse dispersion coefficient (L^2/T), and C is solute concentration at (x, y) (M/L^3).

An observation point with the known concentration is assumed at location x=0, y=0 with a uniform flow velocity at a rate v_x parallel to the x axis. Then, a solute is represented by a concentration C_0 at a rate Q over the aquifer thickness, b. The equation to calculate the concentration on a distance from the observation point can be found from a Green function (Bear 2013) for the injection of a unit amount of a contaminant, under consideration of steady-state conditions, as:

$$C(x,y) = \frac{C_0\left(\frac{Q}{b}\right)}{4\pi(D_L D_T)^{0.5}} \exp\left(\frac{v_x x}{2D_L}\right) K_0\left(\frac{{v_x}^2}{4D_L}\left(\frac{x^2}{D_L} + \frac{y^2}{4D_T}\right)\right)^{0.5} \tag{8}$$

Where K_0 is the modified Bessell function of the second kind and zero order, Q is the rate that the contaminant is injected, b is the thickness of the aquifer over which the contaminant is injected

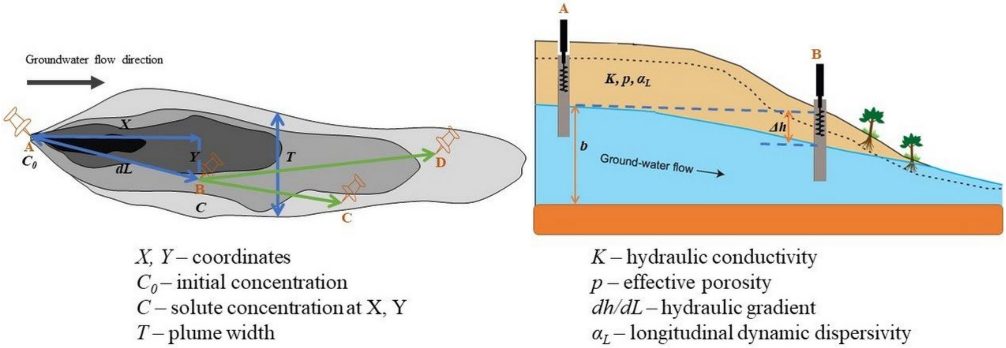


Figure 9 Conceptual framework of the analytical contamination and fate transport model (Paper III)

The analytical solution of the contaminant transport problem (Eqn. 8) in 2D may be calculated via Plume2DSS() add-in (Renshaw 2013) in Excel. However, this add-in requires exact values of transport parameters, which are unavailable at the site. Thus, an optimizer using Macro in Visual Basic for Application (VBA) in Excel was developed (Naseri-Rad et al. 2021). This Macro runs the Plume2DSS() together with the optimizer multiple times with the given range of transport parameter values to minimize the absolute error (the difference between measured and calculated concentration values at each specific point) for each measurement event. The model was assigned by the following characteristics: the exact locations of sampling points (x, y, and dL), obtained from the groundwater model; contaminant concentrations; hydraulic gradients between any two wells; and ranges of value changes for transport parameters, i.e., T, b, K, dh, p, α_L, and α_T. The developed code then calculates the concentration at any point downstream by optimizing the calibration parameters in the given range to minimize the error. Once optimal parameters are determined, the model is validated by using these in the Plume2DSS() add-in, and subsequent comparison between $C_{calculated}$ (a concentration, obtained without running the code) and $C_{measured}$. Thus, optimal transport parameters are numerically obtained via minimization of the absolute error.

As a final step of the procedure, a fate transport modeling was carried out. After all parameters of the case study were defined, new coordinates ($x+x_i$, $y+y_i$, and dL_i) were assigned via extension of already used pathways (an example is shown in Figure 9 for the pathways BD and/or BC) and running a solver for Eqn. 8 to obtain C_i ($x+x_i$, $y+y_i$) in the place where consumers exist.

2.3 Limitations of this study

The main limitations belonged to accessibility and availability to the study area, including investigation of the wastewater treatment unit performance, detailed investigations of effluents and groundwater characteristics via potential measurements performed by the author. Official requests to the head offices of enterprises were ignored; while the informal agreements to perform field tests were later terminated.

There is a limitation in the assessment of the presence of phenol in the case study, as it is important to pay special attention to toxic substances. The limit of the concentration of phenols is 0.25 mg/L according to Kazakhstani standard for the parameter named “phenol index”. The same value is established in the standard of the factory for the observed wells. At the same time, protocols of GW quality measurements name this parameter as “volatile phenols”. This type of phenolic compounds is limited by 0.001 mg/L according to Kazakhstani standards. Thus, there is an unclear situation of which parameter should be used to evaluate the related fate.

The study of groundwater was affected by the relevant lack of data, and multiple assumptions had to be used instead. The fluctuations of the groundwater table were given only for boreholes around the pond. Other fluctuations were not accessible, what limits to build of a transient model. The boundary conditions were manipulative. The values of hydraulic conductivity and conductance from the report varied significantly over the study area. The formation-aquifer is complex, however, for simplification the layer was assumed as one-layer.

There was no critical information available on the initial concentration of TPH in the pond and such an important parameter for contamination transport, as longitudal dispersivity. Also, there were no opportunities to perform respective investigations and measurements, and to obtain detailed data about TPH characteristics and to identify their degradation properties, etc. Thus, there was no opportunity to perform very accurate contamination transport modeling.

As the detailed content of TPH in this certain case study was not known, there was decided to follow the example from Total Petroleum Hydrocarbon Criteria Working

Group and to assume that TPH are not degradable (Gustafson et al. 1997). Consequently, degradation characteristics were assumed as negligible.

Parameter uncertainty will always be a major concern. But the purpose of this study was to provide a tool that gives a picture of contaminant transport and fate by illustrating the patterns of change in contaminant concentration in space with the following assessment for potential fate for environment and people. A detailed discussion about sensitivity and uncertainty analysis, calibration, and validation of the model was beyond the scope of this study.

Finally, all research is limited by time and resources. Some important parts of interest were not covered in this study, e.g., detailed investigations of suitable treatment methods, modeling of water re-use schemes for refineries, cost-benefit analysis for potential modernization and remediation activities, etc.

3 Results and Discussion

3.1 *Status-quo* in the sector in Kazakhstan (Paper I)

It is clearly seen from Figure 10 that legislation and related standards regulate all water use processes in the oil refinery sector in Kazakhstan. Despite this, the problem of environmental pollution exists due to refinery activities. It was found that mismanagement loopholes exist on each step of water use in the industry. Discharge limits for each oil refinery are established separately between the plant and the government. It allows a factory to determine the quality parameters of wastewater (Table 1). When the permissible concentrations of pollutants in discharging wastewater are established, the calculation approach is based on the following: 1) projected and actual purposes of the recipient – reception and accumulation of wastewater from the plant. It means that if the pond is not used as a source of water for agricultural and domestic purposes, 2) it is possible to discharge polluted wastewater with existing concentrations of different contaminants if those concentrations do not exceed the permissible values in the pond. The reason with already high concentrations of pollutants in the recipient is a result of a time lag between the start of contaminated water discharge by the factories and start of the work of treatment units.

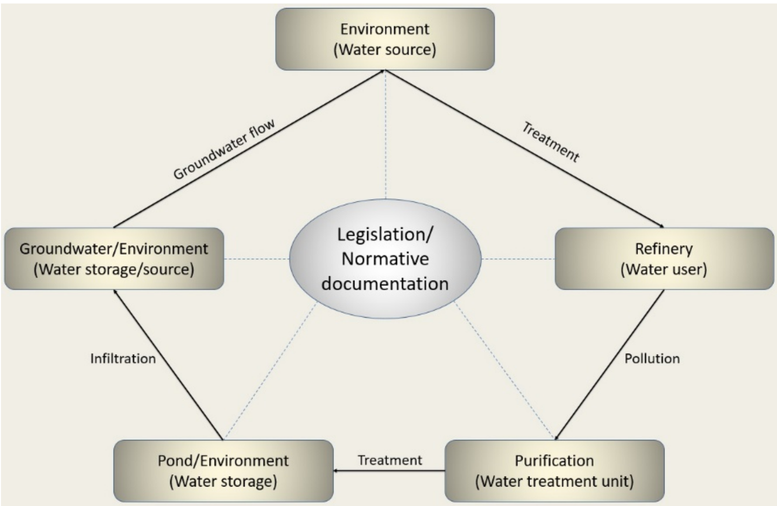


Figure 10 An existing framework for water use in oil refinery in Kazakhstan (Paper I)

Table 1. Maximally permitted concentrations of different parameters in effluent of three Kazakhstan oil refineries (Paper I)

PARAMETER	UNITS	REFINERY X	REFINERY Y	REFINERY Z
Ammonia (NH_4^+)	mg/L	55.18	8.0	4.53
Total petroleum hydrocarbons (TPH)	mg/L	3.02	8.0	2.03
Biochemical consumption of Oxygen (BOD)	mgO_2/L	17.82	16.6	11.6
Nitrates (NO_3^-)	mg/L	19.2	7.8	8.96
Nitrites (NO_2^-)	mg/L	7.7	0.5	-
Sulphates (SO_4^{2-})	mg/L	643.0	500.0	471.1
Phenol's index	mg/L	0.25	0.05	0.182
Chlorides (Cl^-)	mg/L	169.8	350.0	678.8
Suspended solids	mg/L	20.98	25.75	6.05
Surfactants	mg/L	0.52	2.80	1.27
Phosphates (PO_4^{3-})	mg/L	1.05	2.0	6.89
Total Dissolved Solids (TDS)	mg/L	Existing concentration	6000	-

"-"- not controlled

Table 2 presents the characteristics of wastewater effluents discharged from the studied refinery during the period between 2014 and 2017. Factory discharges wastewater with an ammonia concentration of approximately 50 mg/L, whilst the normal concentration of ammonia for municipal effluents is equal to no more than 2.0 mg/L. The same situation is found for TPH. The concentration of TPH in effluents is about 1.2 mg/L, while the limit for the concentration in treated municipal wastewater is 0.1 mg/L. The concentration of BOD is about 10.6 mgO_2/L, while the allowed concentration for municipal wastewater is 3.0 mgO_2/L.

Table 2. Concentrations of different parameters in effluents from the studied refinery (Paper I)

PARAMETER	UNITS	RANGE	MEDIAN	MEAN	STD. DEVIATION
Chlorides (Cl^-)	mg/L	49.80-135.04	70.61	82.48	26.47
Nitrites (NO_2^-)	mg/L	0.08-4.37	0.43	0.10	1.27
Sulphates (SO_4^{2-})	mg/L	238.3-588.7	469.5	449.0	91.0
Nitrates (NO_3^-)	mg/L	1.77-16.41	13.23	12.49	3.96
Ammonia (NH_4^+)	mg/L	38.56-54.34	52.36	49.26	5.97
Total Petroleum Hydrocarbons (TPH)	mg/L	0.68-2.15	1.23	1.30	0.40
Phenol's index	mg/L	0.01-0.03	0.02	0.02	0.01
Suspended solids	mg/L	4.40-9.10	7.69	7.29	1.35
Surfactants	mg/L	0.20-0.45	0.36	0.34	0.08
Biochemical oxygen demand (BOD)	mgO_2/L	8.51-13.12	10.56	10.60	1.48

3.2 Groundwater contamination (Paper II and III)

3.2.1 Groundwater quality parameters (Paper II)

Table 3 presents the results of measurements of groundwater quality from the wells surrounding the recipient pond. Kazakhstani and WHO standards for drinking water were used for assessing all parameters.

Table 3. Water quality parameters for groundwater samples from the observed wells. All units are in mg/L, excluding pH (pH unit) and total hardness (mmol/L) (Paper II)

PARA-ME-TERS	WHO LIMITS	KZ LIMITS		W1	W2	W3	W4	W5	W6	W7	W8	W9
pH	6.5-8.5	6-9	Range	7.2-8.8	7.5-9.0	8.0-9.1	7.9-9.3	8.5-9.5	8.7-9.5	6.9-9.1	8.3-9.1	6.9-8.7
			Mean	8.3	8.2	8.6	8.8	8.8	9.0	8.6	8.7	8.1
			SD	0.4	0.5	0.4	0.4	0.3	0.2	0.6	0.2	0.7
TPH	0.1	0.1	Range	0.16-1.04	0.11-1.40	0.09-0.60	0.11-0.84	0.08-1.20	0.14-0.67	0.23-0.78	0.11-0.99	0.26-0.84
			Mean	0.44	0.41	0.29	0.39	0.40	0.41	0.51	0.45	0.52
			SD	0.25	0.38	0.14	0.24	0.33	0.17	0.19	0.28	0.18
TDS	1000	1000	Range	846-1582	4728-7727	1346-2224	643-2919	899-1450	683-1402	1244-1933	1157-1927	28202-36392
			Mean	1156	6307	1779	2072	1218	1046	1485	1470	31848
			SD	185	952	299	561	172	203	205	298	2922
Cl^-	250	350	Range	98-211	2450-4410	150-520	56-715	160-4410	110-200	150-370	180-798	10000-24757
			Mean	158	3285	256	425	549	172	256	322	14797
			SD	32	577	90	165	1161	24	62	150	3372
SO_4^{2-}	250	500	Range	94-210	544-1300	252-520	127-1100	89-284	150-849	214-296	305-443	4126-9400
			Mean	164	974	379	670	208	298	260	351	7040
			SD	33	190	85	231	46	179	22	39	2086
Phe-nols**	-	0.25/0.001	Range	0.00-0.04	0.00-0.01	0.00-0.06	0.00-0.06	0.00-0.06	0.00-0.06	0.00-0.05	0.00-0.05	0.00-0.12
			Mean	0.01	0.00	0.01	0.01	0.01	0.01	0.01	0.01	0.02
			SD	0.01	0.00	0.01	0.02	0.02	0.02	0.01	0.01	0.04
NH_4^+	1.5	2	Range	0.0-1.0	0.0-27.1	0.0-0.8	0.0-0.6	0.0-8.6	0.0-5.6	0.0-8.8	0.0-10.9	0.0-25.8
			Mean	0.4	2.8	0.3	0.3	0.9	0.7	1.0	1.2	5.6
			SD	0.3	7.4	0.3	0.2	2.3	1.5	2.4	2.9	7.9
NO_2^-	3	3	Range	0.0-0.6	0.0-2.0	0.0-1.1	0.0-0.7	0.0-0.4	0.0-0.4	0.0-0.7	0.0-0.9	0.0-14.5
			Mean	0.1	0.2	0.2	0.1	0.1	0.1	0.2	0.1	1.5
			SD	0.2	0.6	0.3	0.2	0.1	0.1	0.2	0.3	4.2
NO_3^-	50	45	Range	0.0-7.5	0.1-4.3	0.1-3.0	0.0-5.0	0.0-5.3	0.0-4.9	0.0-4.3	0.0-4.1	0.0-21.0
			Mean	2.3	1.7	0.9	1.5	1.8	0.9	1.3	1.5	7.7
			SD	2.9	1.2	0.9	1.6	1.9	1.4	1.6	1.6	8.1
PO_4^{3-}	-	3.5	Range	0.00-0.75	0.00-0.26	0.00-0.20	0.00-1.00	0.00-0.68	0.00-0.41	0.00-0.21	0.00-0.76	0.00-0.08
			Mean	0.11	0.04	0.05	0.10	0.10	0.06	0.06	0.10	0.03
			SD	0.21	0.07	0.06	0.27	0.18	0.11	0.07	0.21	0.02
CO_3^{2-}	-	-	Range	0-48	0-15	0-87	5-59	6-36	13-84	0-137	0-73	0-45
			Mean	15	6	30	32	20	31	39	26	11
			SD	15	5	28	17	8	18	37	19	13
HCO_3^-	384***	-	Range	189-494	14-391	329-709	43-514	262-512	201-346	9-578	210-329	66-464
			Mean	375	119	537	326	343	277	374	264	201
			SD	92	126	100	110	74	42	176	37	138
TH	-	7.0	Range	3.7-12.5	6.2-67.9	3.2-9.8	3.0-12.0	2.1-5.0	2.0-4.8	2.4-9.3	2.8-15.1	219.0-390.0
			Mean	7.6	54.0	6.8	7.6	3.9	3.8	6.5	6.5	272.0
			SD	2.0	15.6	1.7	2.6	0.9	0.9	1.7	3.5	55.0
Ca^{2+}	100	-	Range	14-116	15-625	6-73	8-138	6-44	5-43	3-137	9-72	97-2844
			Mean	39	135	21	29	14	13	27	20	497
			SD	30	154	17	34	10	10	36	16	714

Mg^{2+}	50	-	Range	17-92	65-680	5-330	31-130	14-88	12-61	25-110	21-200	382-4422
			Mean	63	499	88	78	42	39	66	66	2697
			SD	20	196	78	32	18	13	25	44	940
K^{+}	12	-	Range	0.1-3.0	0.0-6.4	0.0-5.0	0.0-6.0	0.0-5.0	0.0-4.0	0.0-6.0	0.0-4.0	0.01-42.0
			Mean	1.5	1.7	1.4	1.6	1.5	1.4	1.8	1.6	14.3
			SD	1.0	2.1	1.6	2.3	1.7	1.2	2.2	1.4	16.2
Na^{+}	200	200	Range	140-230	605-1414	390-685	66-775	220-540	200-500	290-560	220-680	5100-9200
			Mean	190	1136	480	545	348	296	390	412	7093
			SD	27	272	85	181	94	77	79	135	1377
Surfactants	-	0.5	Range	0.1-0.7	0.2-0.6	0.1-0.6	0.0-0.4	0.0-0.4	0.0-0.8	0.3-0.9	0.0-0.4	0.3-1.4
			Mean	0.4	0.3	0.4	0.2	0.2	0.2	0.6	0.1	1.0
			SD	0.2	0.1	0.2	0.1	0.1	0.2	0.2	0.1	0.3
CO_2	-	-	Range	0-37	0-22	0-29	0-15	0	0	0-23	0-2	0-32
			Mean	5	5	4	1	0	0	2	0	7
			SD	11	7	9	4	0	0	6	1	12

- non-described
* WHO does not cover all chemical contaminants in the guidelines, but only those, which pose a risk in a high level (Gadgil 1998).
** EPA, EU and WHO present a range of phenol-derivatives according their toxicity rate. Kazakhstani standard assumes “phenols” as phenolic compounds, which evaporate under high temperature (Angelino and Gennaro 1997).
*** from WHO Guidelines for drinking water quality (1984)

As shown, all wells had exceeding concentrations of total petroleum hydrocarbons (see also Figure 11). While the permissible concentration of TPH is 0.1 mg/L, the concentrations of TPH varied between 0.08 and 1.20 mg/L with the mean value 0.42 mg/L, which exceeded the norm 4 times. Although low concentrations of TPH in water might be considered harmless, researchers found that long-term exposure to TPH causes carcinogenic diseases (Pinedo et al. 2013). Table 3 also shows that dangerous concentrations of phenols were identified in all nine wells. This pollutant has been defined as very toxic and was included in the list of priority pollutants by Environmental protection agency (EPA 2012). The number of disorders has been discovered by acute exposure of phenol: muscular convulsions, hypothermia, muscle weakness and tremor, collapse, and coma etc. (Nair et al. 2008). Measured TDS values exceeded the KZ and WHO maximum permissible levels of 1000 mg/L in most cases on average 5 times (Figure 11). Further, the total hardness in the groundwater samples ranged between 2 and 390 mmol/L with a mean exceeding the standard 6 times (Figure 11). According the Todd classification, almost all samples might be categorized as very hard water. Hard water may cause cerebrovascular and cardiovascular diseases (Stambuk-Giljanovic and Stambuk 2005). The chloride ion presence were between 56 and 24757 mg/L, with most samples elevated WHO’s 250 mg/L recommended limit (exceeding 9 times on average) (Figure 11). There are possible health-related concerns regarding Na^{+} content in the groundwater because the mean elevated concentrations in the wells were 6 times over the permissible KZ limits and WHO indirect recommendation (Figure 11). Consumption of high amount of sodium has been correlated with cardiovascular disease, such hypertension and stroke (Lucas et al. 2011). Finally, individual exceedings of surfactants were identified. Such high levels of surfactants are related to several potential problems. The presence of some surfactants in connection with other contaminants may decrease the biodegradation rate of contaminant or stops the process at all. Moreover, special focus should be paid to Well 9 which had extremely high values. For example, TDS had a value 37 times above the limit, chloride 99 times higher than limit, sulphate exceeded the limit 38 times, total hardness with associated cations by 56 times as well as highly elevated concentrations of ammonia, nitrites, nitrates, potassium, sodium, and surfactants (Table 3). The water containing such levels of those substances would normally be rejected by consumers for any reasons.

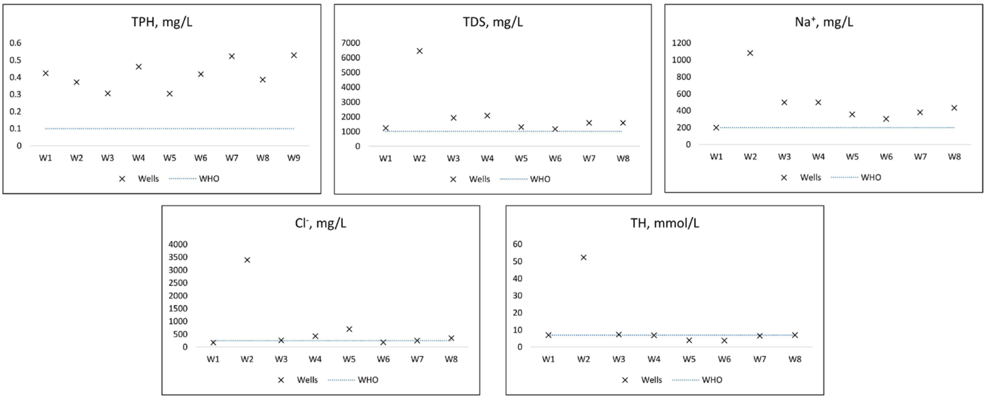


Figure 11 Mean concentrations of some chemicals in the groundwater wells compared to WHO limits (Paper II)

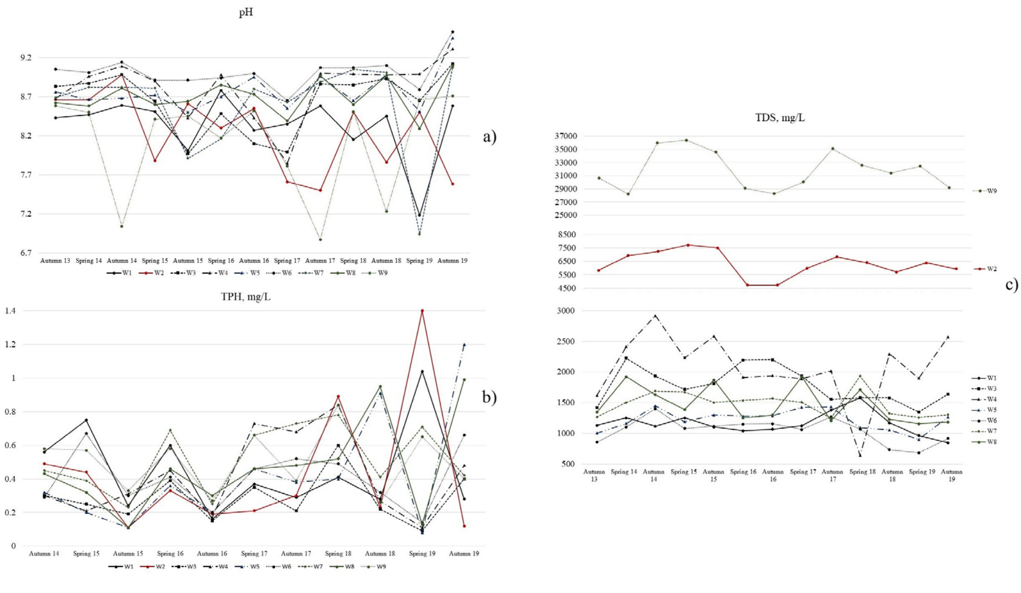


Figure 12 Temporal variation of (a) pH, (b) TPH, and (c) TDS (Paper II)

3.2.2 Multivariate statistical analysis (Paper II)

The correlation matrix was employed for all 117 measurements for determining the loads of the principal components (PCs) shown in Table 4. The first six PCs were selected for the following reasons as variables of dimensionality reduction: the six PCs together gave a cumulative contribution of 78.34%, which is typically regarded as being sufficiently high; the eigenvalues of these PCs are all greater than 1.0 and, according to the Kaiser criterion these PCs must be chosen (Kaiser 1958). The factors can be conditionally divided into two groups. First group accounts to 52.34% of the total variance and is represented by Factors 1 and 2. Usually, the parameters, belonging to those factors, characterize natural conditions of the groundwater. Factors 3-6 contribute to 26% of the total variance and can be categorized, as anthropogenically appeared factors. The natural factor is characterized by high weight values of TH, Ca^{2+}, Mg^{2+}, TDS, Na^{+}, K^{+}, Cl^{-}, SO_4^{2-}, pH, CO_3^{2-}, and CO_2. These results show that the groundwater has suffered serious mineralization process from the natural condition of the salt pond (Allen and Suchy 2001). Also, the correlation matrix indicates the existence of non-carbonate, or constant hardness, ($MeSO_4$, $MeCl_2$, where Me – Ca, Mg), which is difficult to remove in the study area. The anthropogenic factors are characterized by NO_2^{-}, NH_4^{+}, TPH, phenols, and PO_4^{3-}. Nitrite ions are semi-product of the natural denitrification/deammonification processes in the groundwater environment (Hiscock et al. 1991), occurred by high concentrations of ammonia in discharges). The amount of ammonia is not degraded during the saturation processes and some traces still presence in the groundwater. TPH and phenols are directly related to the specification of petrochemical wastewater. As the rocks and fertilizers are absent in the study area (Rao and Prasad 1997), phosphate ions are associated with a vast number of washing processes, which leads to big consumption of different detergents, which contain phosphate substances. Hence, the loading of the contaminant is an indicator of anthropogenic impact on the groundwater.

Table 4. Factor loadings (Varimax normalized) (Paper II)

	NATURAL		ANTHROPOGENIC			
VARIABLE	**FACTOR (1)**	**FACTOR (2)**	**FACTOR (3)**	**FACTOR (4)**	**FACTOR (5)**	**FACTOR (6)**
pH	-0.233	**-0.900**	-0.045	0.042	0.023	0.014
TPH	0.102	-0.034	-0.267	**0.746**	-0.024	-0.201
TDS	**0.924**	0.205	0.171	0.158	-0.002	-0.058
Cl^-	**0.888**	0.251	0.203	0.146	-0.086	-0.058
SO_4^{2-}	**0.927**	0.086	0.203	0.063	0.041	-0.046
NH_4^+	0.289	-0.045	0.198	**0.783**	-0.051	0.162
NO_2^-	0.254	-0.059	**0.797**	-0.075	-0.173	-0.004
NO_3^-	0.514	0.012	0.500	-0.031	0.363	0.121
PO_4^{3-}	-0.100	0.041	0.012	-0.039	0.027	**0.886**
CO_3^{2-}	-0.140	**-0.692**	-0.074	-0.010	-0.023	-0.337
HCO_3^-	-0.297	-0.159	-0.120	0.026	0.460	0.208
TH	**0.927**	0.160	0.147	0.188	0.053	-0.033
Ca^{2+}	**0.729**	-0.069	-0.382	-0.182	-0.231	0.092
Mg^{2+}	**0.798**	0.215	0.326	0.313	0.085	-0.050
K^+	**0.807**	-0.032	-0.375	-0.106	0.008	0.039
Na^+	**0.931**	0.150	0.196	0.133	-0.004	-0.045
Surfactants	**0.732**	0.131	0.107	0.165	0.085	-0.116
CO_2	0.094	**0.845**	-0.133	-0.025	-0.013	-0.165
Phenol	0.196	0.078	-0.015	-0.077	**0.873**	-0.086
Eigenvalue	7.984	1.960	1.458	1.307	1.160	1.015
% of Variance	42.023	10.315	7.676	6.881	6.105	5.340
Cumulative %	42.023	52.337	60.013	66.894	73.000	78.339

Based on the performed CA and results above, the study area was divided into three clusters. Cluster 1 combines observed wells W9 and W2. These wells are recognized as highly contaminated with the highest exceeding of many chemical parameters. They have similarities in the distribution of pH, which is followed by host geology. The wells are situated on the south-west site from the pond and probably approve an assumption about direction of groundwater flow. Cluster 2 is formed by wells W7, W8, W1, and W3. These wells are located on the south and west sides of the pond and characterized by twofold characteristics: firstly, significant pollution rate, including the same concentrations of the TDS and TDS related chemicals, and secondly, the equal temporal distribution of pH. It means that groundwater on that site is affected by pollutant transport from the pond in the same manner. Finally, Cluster 3 is represented by wells W6, W4, and W5. All wells are located north of the pond and are characterized by lower concentrations of the pollutants compared to other wells.

Thus, the results of the multivariate statistical analysis indicate that pollution spread out of the sanitary zone to the west direction from the recipient pond and potentially could create hazard for rural inhabitants. Moreover, the trends of TPH pollution tend to rise in time (Figure 12). It potentially says that the pollution problem is growing in the area.

3.2.3 Heckman selection model (Paper II)

Table 5 shows the selected variables used in this analysis and their descriptive statistics. According the Kazakhstani sanitary and epidemiological requirements (Kazakhstan 2015), TH, TPH, and Na^+ are considered hazardous for public health and rated with value 1.0 for the variable D_i. TDS, sulphates, and chlorides are considered as non-toxic and were rated as value 0.0 for the variable D_i. TDS, Cl^-, SO_4^{2-}, Na^+, TH, and TPH were encrypted in the matrix of variables as “1”, “2”, “3”, “4”, “5” and “6”, respectively.

Table 5. Selected variables characteristics* (Paper II)

VARIABLE	TOXIC	NON-TOXIC
Number of observations	324	351
	48.0%	52.0%
Number (%) of exceeded values (Std.Dev.)	255 (78.7)	248 (70.7)
Dependent variables		
Toxic contaminant	1.0	0.0
% of exceeding	664 (1042)	862 (1526)

*descriptive statistics of chosen chemicals is available from Table 3

Table 6 presents the results of the Heckman selection model. Rho has a positive value, which means that it is possible to estimate relationships between chosen variables and final contamination. All variables, excluding number of well (which represents location of the wells), are considered significant. The concentration of pollutants has the greatest influence on the total contamination. A positive value shows a high likelihood of potential hazards for people's health. Obviously, high concentrations of pollutants might lead to deterioration of health, especially during long-term exposure. In the studied case, 503 of 675 values exceed acceptable limits by 7-8 times in average. The variable of toxicity rate is the second significant factor. This variable reflects to lower percentage of exceedings for toxic contaminants than for non-toxic, instead of higher number of exceeded values for toxic contaminants than non-toxic. The hypothesis is that even if the concentration of the toxic contaminant exceeds the standard by just a few units, the toxic properties could be much more dangerous for human health, compared to the consumption of highly polluted water by non-toxic contaminants. The independent chemicals represent the third significant variable. Individual characteristics of chosen chemicals are explained in sub-section “Groundwater quality parameters”. The location of the well is rated as a non significant parameter. Nevertheless, the investigation of hydrogeological characteristics deserves attention to determine the spread of contamination.

Table 6. Estimated results of the Heckman selection model (two-step) for selected chemicals (Paper II)

VARIABLE	COEFFICIENT	STD. ERR.	Z-STATISTIC
Chemical	-0.156	0.074	-2.11
Concentration	1.576	0.260	6.07
Toxicity rate	0.789	0.245	3.22
Number of well	0.020	0.025	0.83
Rho		1.0	

Thus, the results of the Heckman selection model indicate that particular focus should be paid to the distribution of toxic contaminants.

3.2.4 Groundwater modeling (Paper III)

The groundwater flow was modeled to identify the pathways of TPH plume movement and to assign the required coordinates for contamination transport modeling. Figure 13 shows the simulated water level contours for steady-state conditions. Results of the calibration reflect the lithology of the area. The higher HK belongs to the territory along the Irtysh river and Upper-Quaternary deposits (aQ_{III}), as they are formed by soils with a high level of water permeability (quartz, sand, gravel, and pebbles, instead of more clayey soils in the eastern direction). The following decrease of HK from northwest to southeast is explained by the local topography, as the groundwater is located deeper, and the clay content variation in the aquifer. The conductance of the drain (river) (50 m^2/d) and boundaries (125 m^2/d) were approximately equal to available data after calibration. The RMSE of modeled groundwater level against measured was 0.64 m and the R^2 coefficient was 0.68. Hence, the model was considered as sufficiently accurate. The MODPATH software was used in this step to evaluate potential flow of the contaminant specifically from the source of the pollution. It showed that the plume moved in a western direction with some displacement towards the southwest. Particle tracking, using MODPATH, showed the potential transport towards agricultural fields, where groundwater is used for irrigation (4.5 km from the pond) and nearby rural areas (Michurino and Pavlodarskoe villages, 8 km from the pond).

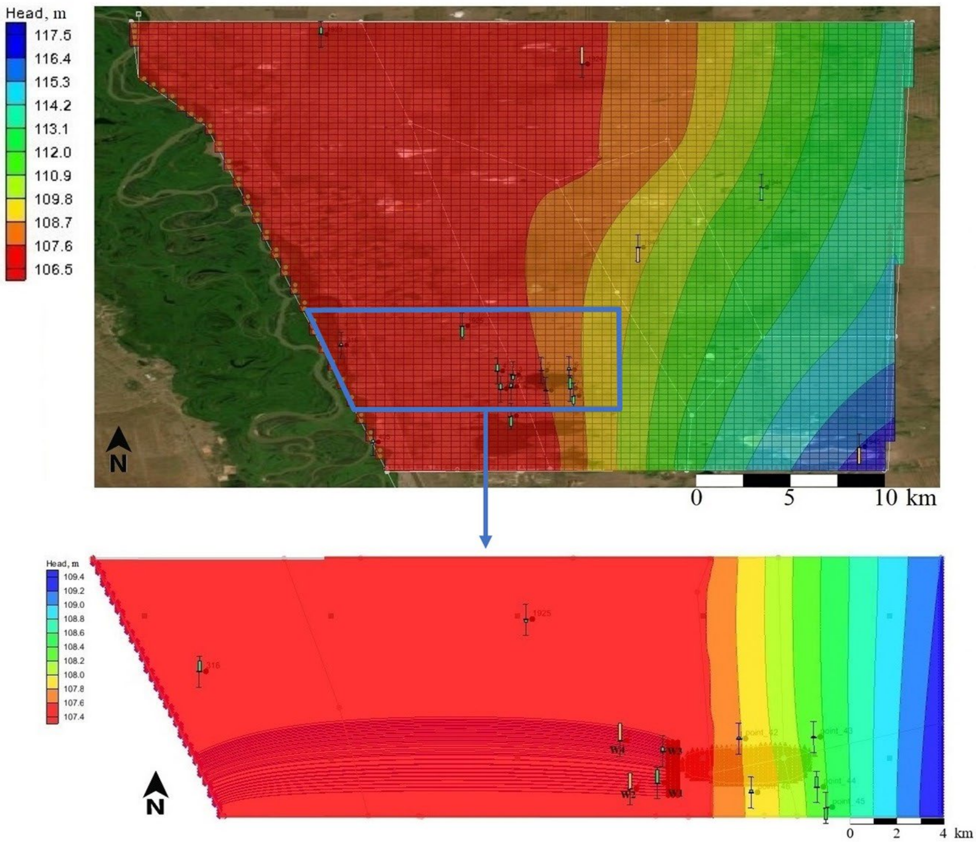


Figure 13 The groundwater flow model (Paper III)

3.2.5 Contamination transport modelling (Paper III)

After calibration of the groundwater model, two pathways, located downstream from the source of pollution, were chosen for the contamination transport modeling. Pathway 1 and 2 (P1 and P2) originated from the monitoring wells W1 and W3, respectively, where coordinates *x*, *y*, and measured concentrations of TPH were established as initial conditions ($x=0$, $y=0$, and C_0). The W2 and W4 are located at the boundary of the sanitation zone (1000 m from the pond), where the concentration of TPH should not exceed a safe limit (100 µg/L) for drinking and domestic purposes according to Kazakhstani legislation (Kazakhstan 2015). Coordinates for W2 and W4 and measured concentrations of TPH were used for calibration of the parameters T, b, p, K, α_L, α_T, and dh for Pathway 1 and 2, respectively. Figure 14 shows the results of the calibration. The R^2 coefficient was equal to 0.9 and indicated good performance of the model. Calculated means for values of Q, b, p and dh were similar in both models: semi-analytical transport and groundwater.

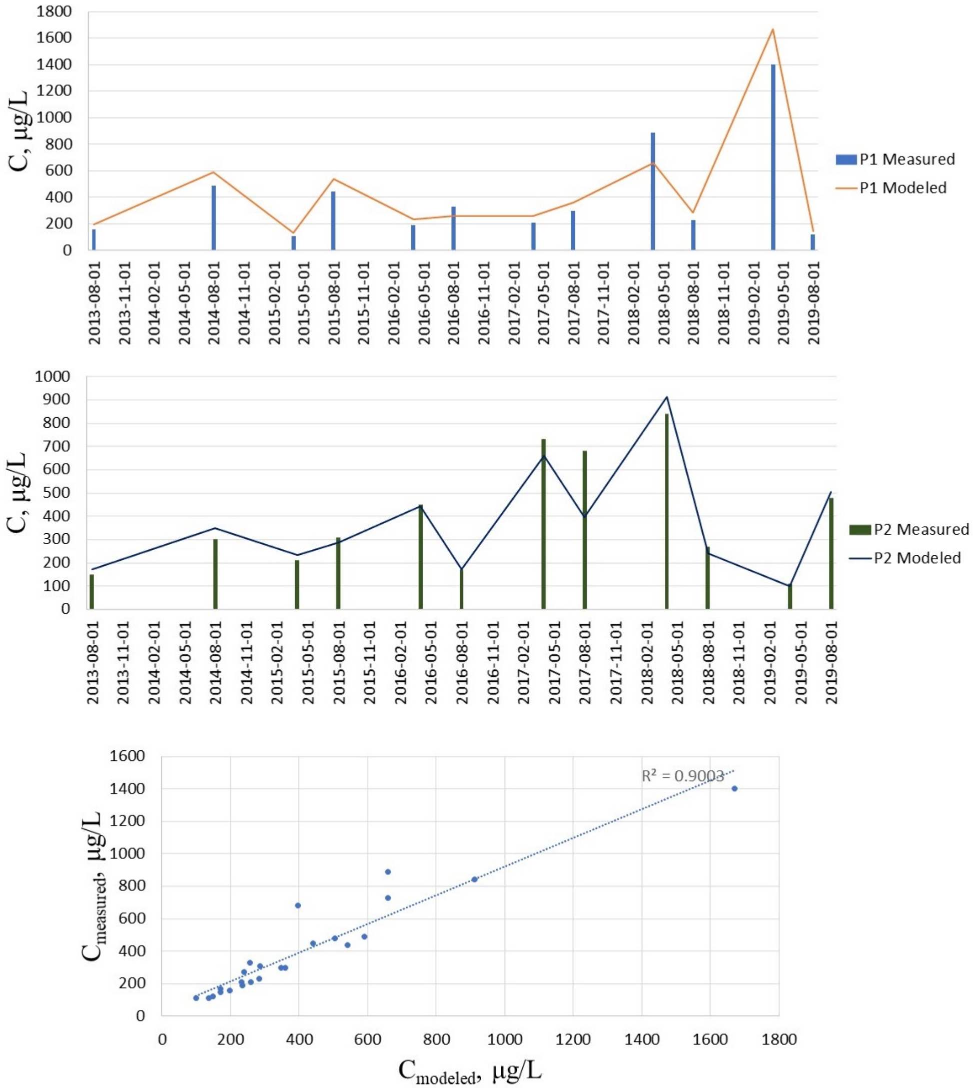


Figure 14 Results of transport contamination model using unified values of the parameters (Paper III)

Figure 15 presents the potential results of the fate transport of contamination, based on measured concentrations in the monitoring wells, and unified transport geological parameters for individual cases and historical scenarios. The distance (dL_i) step was assumed as the square root of x+100 and y+20 m from the starting observation points. The dh_i was estimated as 0.01 m for each dL_i step, based on the GW model. Obviously, the plume width correlates with the starting concentrations. The potential maximum distribution during the spring season in 2019 and 2018 was 6 and 3 km for Pathway 1 and 2, respectively. The starting concentrations (C_0) showed maximum historical values in those years. The same situation was found for the autumn periods when the potential maximum spreading of the contamination was 4.5 and 2.6 km for Pathway 1 and 2, respectively. The calculated distance is higher during the spring seasons compared to the autumn. Lower values of the calculated plume fit the lower concentrations with a resulting shorter distance from the origin of pollution. However, even for these cases, the distance was relatively large, almost 1.2 km from the source of the contamination.

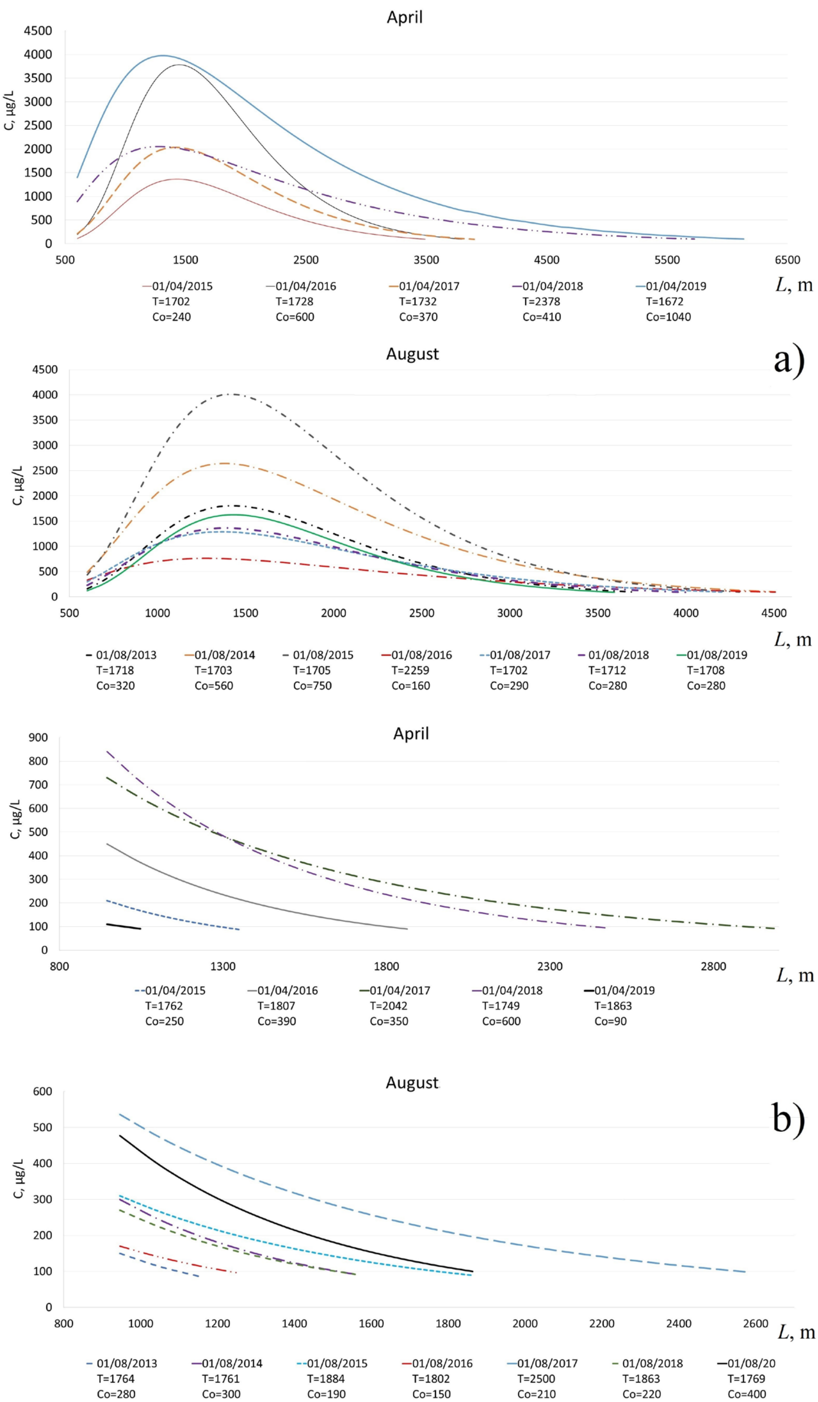
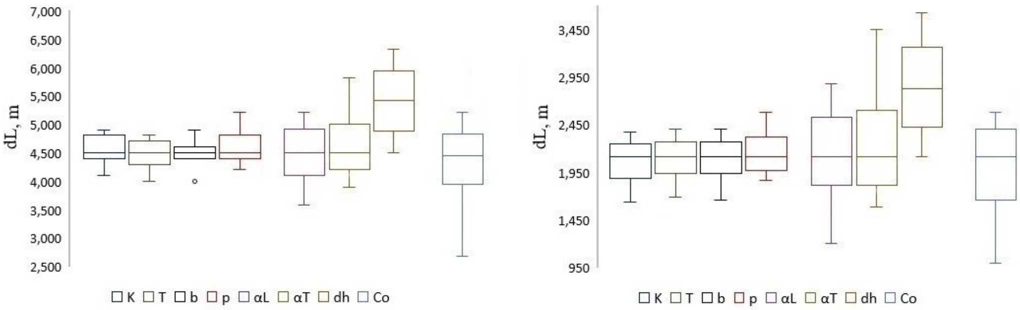


Figure 15 Modeled contamination depending on distance (in m) from a) W1 and b) W3 (Paper III)

The final step of the application is the analysis of parameters' sensitivity. The ranges for *K*, *T*, *b*, and *p* were changed several times in an equal manner: they were decreased by 25% and 50% and increased by 25% and 50%. For the investigation of the relationships between *dh* and dL_i, the range for *dh* was considered between 0.01 and 0.1 m. The C_0 was assumed as 500 µg/L for all scenarios. To assess the potential spread of plume, depending on the initial load of the TPH, the range for C_0 was considered between 50 and 1000 µg/L. After establishing new values, dL_i was calculated to the extent, when the concentration of TPH is considered safe. The results are presented in Figure 16. While all parameters show relevant changes in the resulting dL_i within the range of change, longitudinal and transverse dynamic dispersivity together with plume width were considered as the most sensitive parameters in this study. This is explained by the fact that these parameters might be changing over time depending on contamination characteristics, while parameters describing geological characteristics are constant. The increase of *dh* causes significant increase in the distance of plume spreading, as it is related to enhanced linear velocity, and consequently, enhanced injection rate of the contaminant. The parameters may vary significantly depending on the scale and characteristics of contaminants. If the C_0 is equal to 1000 µg/L, the affected zone can spread 5 km for P1 and 2.5 km for P2. The highest rate of the spreading belongs to the area near the source of pollution, e.g., the growth of the initial concentrations from 100 to 150 µg/L causes extension of the plume spread corresponding to 0.25 km (from 1.30 to 1.55 km) for P2, while the following dL_i is changed for 120-50 m for each 50 µg/L.



a) b)

Figure 16 Sensitivity analysis for a) Pathway 1 and b) Pathway 2 (Paper III)

Thus, the results of environmental fate assessment show that the contamination likely has spread out 2-6 km from the recipient pond of wastewater from the studied refinery. Future data acquisition for the most sensitive parameters is required to better control the situation of the GW contamination in the region.

3.3 Lessons and implementation (Paper IV)

The problem of water contamination by petroleum refineries is not unique for Kazakhstan but exists worldwide. Currently, there is still not full confidence in the “safety” of partly treated wastewater for two reasons. Firstly, the fate of hydrocarbons has not yet been fully explored. For example, the recent study of PAHs degradation shows that the products of degradation also are hazardous (CONCAWE 2020). It means that even low concentrations of persistent substances discharged into the environment can create a hazard. Secondly, several refineries still show high concentrations of contaminants, permanently or accidentally, which requires additional investigations. For instance, while there is a positive trend of decreasing of hydrocarbons in refineries’ effluents in Europe, the mean annual concentration of TPH among the refineries equals 1.4 mg/L for all European refineries with maximal concentration 16 mg/L.

This study identified that effective policy is an efficient *response* to achieve the sustainable water use in the oil refinery sector in Kazakhstan (Figure 17). The best option to assure safe water is efficient water and wastewater management of water users, instead of post-factum attempts to clean already polluted sources. The management includes appropriate technology standards coupled with sufficient operational monitoring, which aims to prevent contamination. Thus, the *response* includes implementation of 1) the concept of circular economy (CE) (via 1a) water reuse and 1b) Best Available Techniques (BAT)); 2) Improved methodology for Environmental Impact Assessment (EIA), aiming to toughen the requirements for wastewater quality and characteristics of their recipients; and 3) Improved system of environmental monitoring.

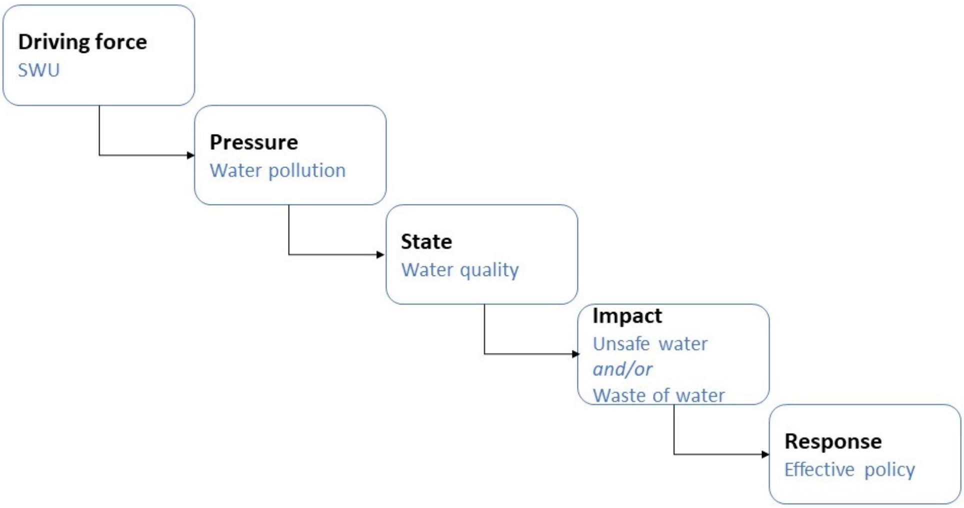


Figure 17 The DPSIR framework for this study

3.3.1 Circular Economy

The core of the CE is the transition to circular form, or 4Rs ("reduction, reuse, recycling, and recovery") approach, when the wastes, generated during the manufacturing process, are recycled, and all resources are re-used again as much as possible (Smol et al. 2020). The importance of wastewater reuse has been highly emphasized in the context of CE with the promotion by relevant legislation (EU 2020).

In comparison with developed countries, refineries in Kazakhstan do not aim to re-use water. Achieving sufficient re-use water quality is impossible without appropriate treatment techniques, which is the core of the BAT approach. The principle of BAT is to find the most efficient and cheapest way to meet the requirements for safe or re-used water. While the industrial processes and content of generated WW are the same for refineries in USA/EU and Kazakhstan, the significant difference between developed countries and Kazakhstan is the usage of the "in-plant control" principle and BAT. It means that there are the requirements not only for finally treated effluents but for the quality of generated WW after each technological unit either. It leads to additional preliminary treatment, which reduces the burden on the final (or "end-of-pipe") treatment system and enhances the efficiency of it. As the generated wastewater consists mainly of salty unprocessed heavy oil-water emulsions, and even after primary mechanical treatment, there is a challenge to remove hydrocarbons from wastewater (Bruno et al. 2020). The basic biological treatment method (activated sludge), which is used by refineries in Kazakhstan, cannot efficiently treat for two reasons: firstly, the petroleum hydrocarbons are heavily degradable, and, secondly, salinity and toxicity of wastewater inhibit the efficiency of biomass. Refineries in the other countries solve this issue by using advanced techniques on each step of treatment: pre-, secondary, and post- (or polishing) treatment.

3.3.2 Environmental Impact Assessment

There are different approaches in Kazakhstan and EU/USA to make the process of implementation of the EIA efficient and transparent. Related decisions are taken by respective policy standards in both cases. However, both the USA and the EU, base their decisions and develop their strategies on the scientific approach (Zijp et al. 2016). The design of policy implementation in the EU has been based on the relevant scientific investigation through the possibility of integrating the respective technological development (Voulvoulis et al. 2017). Winans et al. (Winans et al. 2017) have emphasised, firstly, that policy actions should be well designed, clearly explained and regularly evaluated; and secondly, experts must be involved in the process of the decision-making to achieve the successful implementation of the EIA.

Furthermore, that is a common situation worldwide when the results of investigations of the impact of oily effluents become available and transparent. Usually, the content of hydrocarbons in the effluents from refineries have been mainly subjected to detailed evaluating their toxic and cancerogenic properties. As a result, it is considered, the effluents are safe if toxicity tests show reasonable results. The current conditions of discharges in the USA and the EU have shown a positive trend in general, as requirements for their content are established based on reliable techniques of the EIA.

In Kazakhstan, the current system of the Environmental Impact Assessment, which establishes the criteria for maximum permissible concentrations of contaminants in wastewater, has obvious gaps. The formal eligibility to pollute already contaminated sites and to establish the MPD equal to a background concentration of the pollutant in the recipient causes environmental and social fate. Also, there is an unusual practice, when the wastewater releases into the ponds with the following affection on groundwater, like in the Kazakhstani case. In contrast, the EU directly forbids the transfer of pollutants from one environmental media to another. Also, it contradicts with the actions needed for safe environment, such as liquidation and remediation of historical contamination, reduction in pollutant emissions, and an increase in volume or recycled and reused water (Naseri-Rad et al. 2020).

3.3.3 Operational monitoring

One more reason, why the contamination still exists is a lack of sufficient operational monitoring. During use and following emission to the environment, petroleum hydrocarbons can be metabolized and degraded to transformation products. Thus, the environment is exposed to an even greater number of chemicals, while only fewer of them are regulated (Van den Brink et al. 2018).While the developed countries identified certain indicators, with the detailed list of pollutants in oily wastewater, such as PAHs (including total PAHs, and individual compounds), benzene, toluene, ethylbenzene, xylenes (BTEX), etc., for better estimation of the toxic effect of their existence in wastewater; Kazakhstani oil refineries monitor only the sum of TPH, without detailed investigation of the resulted effect on the environment. Still, mentioned petroleum compounds are not degradable, which might cause risks even at low concentrations. Continuous update of the list of substances for operational control during the wastewater treatment and environmental monitoring in developed countries ensures environmental safety and follows the sustainable development principles positively affecting the monitoring system. For example US EPA carries out permanent control of the quality of wastewater and recipients to detect any accidental or other exceedance of permissible values for contaminants. In the EU, any operator of pollution monitors their emissions under the directives on industrial emission and integrated pollution prevention and control.

Multiple barriers, such as perception of the industry of pricing and technological changes, slow down the process of implementation the suggested *responses* in the oil refineries in Kazakhstan. Currently, the price of water is very low for the industry, as well are the penalties for the violation of the current version of the law. Thus, there is no engine to initiate the transition towards the circular economy for industries yet. Also, a jump into the modern variety of new technologies for treatment can give the options to choose efficient and cheap treatment approaches.

Changing the policy, which has not been updated for years, is a real necessity for today. Identified gaps in the legislation, which lets to discharge inappropriately treated wastewater, should be revised via implementation of suggested principles.

4 Conclusions

The results, presented in this thesis, address the established objectives, as follows:

Objective A: to investigate water and wastewater management at the oil refinery factories in Kazakhstan in accordance with respective national and international legislation.

This study identified the imperfections of the existing framework for water use in the sector in Kazakhstan. It was found that there is no incentive by current law in Kazakhstan to shift towards the SWU, as there is in developed countries where enforcement of legislation was the first step towards the SWU. Formally, environmental regulation in Kazakhstan promotes the *polluter pays* principle and follows the World Health Organization (WHO) recommendations for ensuring drinking water quality, including groundwater. Simultaneously, the weakness of legislation was identified by lacking unified and transparent standards for treatment processes, and wastewater quality. Low water fees, low penalties for pollution, and legislative loopholes, such as a possibility to establish permissible values for concentrations of the pollutants in wastewater equal to background concentration of the pollutant in an already polluted recipient, allows the situation to remain unchanged. Thus, Kazakhstani standards are not sufficiently adapted for international guidelines, which causes the release of potentially toxic substances together with wastewater into environmental media, where those substances migrate into another, e.g. groundwater. The situation creates a hazard of presence of toxic chemicals, and subsequent transport of contamination with a potential negative impact on public health. The water-saving potential in Kazakhstan is ranked as one of the major opportunities in the water sector, especially for the industry, where the aim is two-fold: reduce pollution and reuse water for technological processes. Thus, this is the only effective way to prevent potential damage to the health of people who use contaminated water.

Objective B: to assess groundwater safety affected by improper treatment of refineries' wastewater.

This study identified that groundwater surrounding the wastewater recipient pond has been affected and containing high level of some chemicals, such as total petroleum hydrocarbons, total hardness, total dissolved solids, and sodium. These pollutants are likely spreading towards areas with substantial groundwater use. Multivariate statistical analysis showed that there is twofold origin of pollution:

anthropogenic and natural. Even though anthropogenic load might be controlled by respective decrease of contamination via effective wastewater treatment, this study showed that man-made chemicals with a high level of toxicity, such as TPH, exist in concentrations exceeding permissible limits on the boundary of the sanitary zone. Heckman selection analysis identified that toxic substances reflects to lower percentage of exceedings for toxic contaminants than for non-toxic, instead of higher number of exceeded values for toxic contaminants than non-toxic. It means that even if the concentration of the toxic contaminant exceeds the standard by just a few units, the toxic properties could be much more dangerous for human health, compared with the consumption of high concentrations of non-toxic contaminants in contaminated water. Thus, special attention should be paid on toxic substances during the related investigations. The development of groundwater flow and contamination transport models is a viable part of the assessment of the pollution pressures on that body. This study focused on potential impact of groundwater contamination by total petroleum hydrocarbons (TPH) in the region. The models were developed to investigate behavior of the plume of TPH inside the aquifer and to give respective recommendations for environmental managers and local habitats. The results, based on historical observations, showed that the risks for residents in the potentially affected rural area of Kazakhstan can be avoided, as the plume has not reached the villages considered to be within the risk zone. However, agricultural areas at 2-6 km downstream the source of pollution could be affected by contaminated water. Moreover, a future growth of the industrial capacity in the region, with expected increase of industrial pollution, does not promise improvement of the groundwater status. As it is shown, the increase of initial concentration of TPH, caused by high loading of TPH from the industry, significantly extends the affected area. Thus, the adverse effect of the possible contamination in connection with the poor monitoring system of such contamination might consider the careful usage of groundwater from the shallow aquifer for irrigation purposes in this area.

Objective C: to define possible solutions for industrial water and wastewater management system in Kazakhstan to ensure the SWU.

In order to achieve the SWU, the system of industrial water and wastewater management relies on legislative and normative standards. In Kazakhstan, the system is weakened not only by gaps in legislation, but also by the absence of appropriate environmental tools (such as operational monitoring, and environmental assessment). The defined criteria to ensure equitable access of different water users and viable mechanisms to achieve water safety are 1) implementation of concept of Circular Economy (CE), via implementation of Best Available Techniques (BAT) and water reuse, 2) improvement of current system of Environmental Impact Assessment, and 3) improvement of the existing scheme of operational monitoring for wastewater quality. The suggested potential solutions should follow the requirement to control the amount of contamination inside the technological processes before final discharge. The performed investigations showed that decision-makers in Kazakhstan, unlike developed countries, do not follow scientifically approved techniques and mechanisms to prevent pollution, which guarantees a good-status of receiving water bodies. The current trend is a transition towards “closed-loop” systems – choosing sufficient treatment methods specifically for each factory, considering environmental conditions, facility size, age of facility, equipment, etc. Refineries in Kazakhstan do not aim to re-use water despite the risk of water scarcity in the region. It is recommended to use an “in-plant control” technique, i.e. installation of extra regeneration units for processing water before the final (or “end-of-pipe”) treatment system to supply regenerated water for secondary use within industrial processes. The result is twofold: decreasing freshwater consumption and enhancing efficiency of the final treatment. It was also found that the current wastewater treatment scheme at oil refineries does not use efficient advanced techniques on each step, including pre-, secondary, and post- (or polishing) treatment. Thus, it is highly emphasized to improve the wastewater treatment systems via implementation of the BAT.

The current scheme of Environmental Impact Assessment in Kazakhstan is weakened by the respective legislative loophole. The adjusted new unconditional requirements for effluents safety assessment, such as a detailed investigation of effluents characteristics using, e.g., Parameter-Specific Approach, Whole Effluent Toxicity (WET) Approach, or Bioassessment Approach toxicity tests have showed high efficiency worldwide. The ban for potential transfer of toxic substances from one environmental media to another (for example, from surface water to groundwater) in many countries has contributed to the environmental improvmenets and promote the both the govenments and the indusrties to follow the SWU.

Kazakhstani oil refineries monitor only the sum of TPH, without detailed investigation of the resulted effect on the environment, while the developed countries identified certain indicators, with the detailed list of pollutants, including toxic, such as PAHs (in total and individual compounds), benzene, toluene, ethylbenzene, xylenes (BTEX), PFAS, etc., for better estimation of the toxic effect of their existence in wastewater. Still, the mentioned petroleum compounds are not degradable, which might cause risks even at low concentrations. Continuous update of list of substances for operational control during the wastewater treatment and environmental monitoring in many countries ensures the environmental safety and follows the sustainable development principles positively affecting the monitoring system. Thus, unconditional requirements for effluent safety, continuous update of the list of the potential pollutants and implementing BAT are the current requirements for the industrial management to follow the SWU.

5 Final remarks and future outlook

This work was to understand, to what extent the water use in the oil refinery industry in Kazakhstan is sustainable and to assess its impacts on the environment. It was found that the current "*status quo*" includes formal approval for polluting activities by the industry, which causes risks for environment and public safety. This situation violates the principles of equitability and bearability of the SWU.

Delivery of SDGs requires a healthy and productive environment. In order to achieve the SWU and to decrease the environmental pollution the following recommendations should be considered:

- This study identified a severe status of the contaminated recipient pond for wastewater from the studied refinery, and a related extended groundwater pollution, which likely will exist for decades and spread out on a km scale. The main action from the government should be to accept that the problem exists, instead of accepting the problem itself.
- Legislative loopholes in the methodology for establishing the requirements for effluents from the refineries is one of the major contributor for the resulting pollution. The government should take a leading role in the development of sufficient requirements for industrial wastewater treatment and disposal systems. The core action is the development of unified, transparent, and fair regulative standards for the procedure of the Environmental Impact Assessment.
- The lack of integration of a scientific-based approach weakens water management practices both at the governmental and industry levels. Detailed investigation of wastewater characteristics, and the application of new tools for environmental monitoring, such as developing groundwater and contamination transport models, will assist the Environmental agencies to assess and control industrial impact and related risks.
- The implementation of the principles of Circular Economy, particularly "water reuse" and "best available techniques", can contribute to preventive activities and reduce the risks for environment and society.

In order to achieve efficiency of the described activities above, communication of the risks to key stakeholders in the government-industry-science is needed.

5.1 Future outlook

Kazakhstan deals with the implementation of suitable legislation. The government of Kazakhstan applies efforts to improve the situation through policy strengthening. A new ecological code has been adapted in the beginning of 2021. The law claims the implementation of BAT, increased penalties and investment of industry into environment protection. The implementation of the law aims the transition to sustainable development and "green economy", with a focus not only on resource efficiency and waste prevention but on human well-being and ecosystem resilience as well. However, there is still concern about its efficiency. A law does not act by itself, but via relevant guidance documents. Special attention in the future should be paid to control mechanisms of implementation of new rules for industrial effluents.

The main focus for future work in the studied area should be paid on characteristics of contamination, such as identification of individual substances, toxicity analysis, and ability to persist in the environment. It is suggested to perform additional investigations of TPH's plume spreading, based on the results of this study, and especially on the results of sensitivity analysis. The persistent and hazardous hydrocarbon fractions and types, such as PAHs and BTEX, should be identified in both wastewater and groundwater for better understanding of the existing impact on environment and public safety. Fieldwork aiming to better understand the characteristics of groundwater flow and transport contamination is considered for future investigations. Also, the recipient pond requires investigations as it has been in operation for more than 30 years. The sediments might potentially contain high concentrations of many dangerous contaminants. The ways of their transfer from one environmental media to another also have to be studied for consideration in the following remediation programs.

Additional epidemiological studies should be conducted in municipalities nearby and downstream the pond to assess potential connections between the high concentrations of some pollutants, such as TPH, phenols, Na^+, Cl^-, SO_4^{2-}, TDS and TH and cardiovascular and oncological diseases in the region.

The method of contamination transport modeling, developed and used in this study, is proposed as an environmental tool for assessment of industrial impact on groundwater and related risks not only in the studied area, but for other similar potential cases with limited data, which is also one of the major weaknesses of the system.

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Paper I

sustainability

MDPI

Review

Pitfalls of Wastewater Treatment in Oil Refinery Enterprises in Kazakhstan—A System Approach

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Abstract: The present article is an assessment of wastewater treatment processes in the oil refinery sector in Kazakhstan by comparing relevant experience of developed and developing countries. The legislation in this sphere, the treatment methods, the discharge process and the effect on the environment were evaluated following international and national regulations. In our study, the wastewater systems in three factories in Kazakhstan were assessed. Results show that, even though the environmental regulation in Kazakhstan promotes the *polluter pays* principle and follows the World Health Organization (WHO) recommendations, the oil refinery plants in Kazakhstan still contain exceeding concentrations of pollutants in their effluents. One issue is that the local legislation allows disposal of wastewater to natural or artificial ponds as long as the concentrations of pollutants in effluents are less than the already existing concentrations in the pond. Consequently, the factories can use ponds with an initially high concentration of contaminants. The high initial concentration of pollutants in the pond water is due to wastewater discharged before the implementation of current environmental regulations. This issue in the current legislation leads to the situation where there is no incentive for efficient wastewater treatment. The national law also lacks regulations regarding which methodology should be used to assess the pollutants in the wastewater. Thus, the control by national environmental office for each enterprise is negotiated separately between the factory and the governmental body. This gives the factory a strong position to define the parameters assessing the effluents. This has led to none of the factories measuring, e.g., heavy metals in discharged wastewater. Total petroleum hydrocarbons (TPH) concentration in wastewater is often exceeded at each factory and there is no analysis done for different hydrocarbon fraction. To overcome the issues described in the present study, we strongly recommended a unified and transparent methodology for the country's oil refinery industry to assess important pollutants in discharged wastewater.

Keywords: industrial wastewater; groundwater; water pollution; oil refinery; legislation; Kazakhstan

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1. Introduction

Modern Kazakhstan is a country with a constantly developing economy and industry is Kazakhstan's economical base, with stable growth during the last 20 years. The refining enterprises also significantly contribute to the structure of industrial development [1]. Kazakhstan is the second biggest oil producer after Russia among the Commonwealth of Independent States countries. The petroleum industry is the major actor and accounted for about 10% of the country's GDP in 2016 [2]. Kazakhstan is one of the key suppliers of hydrocarbon raw materials for the world economy. In 2016, Kazakhstan was rated 16th in the world with a production volume of 79.3 million tons of oil and gas condensate (representing 2% of the global production). The refinery throughput in Kazakhstan is 339 thousand barrels daily, a number that is growing by 4.6% every year. The refinery capacity is estimated to be 350 thousand barrels daily [3].

Water is a very important reagent in petroleum and petrochemical production processes. Distillation, extraction, preparation of solutions, cooling systems and washing processes are some examples of industrial water use [4], leading to a large consumption in the current fuel and electricity production. The total water consumption for those purposes is projected to increase by 55% between 2000 and 2055 globally [5].

The total water consumption in the Republic of Kazakhstan in 2016 was estimated to be 24.7 km^3, including 5.23 km^3 (representing about 20%) for industrial needs. The largest share of the industrial water use is found in heat power engineering, non-ferrous metallurgy, and the oil industry [6].

Historically, the oil refinery industry has been associated with groundwater pollution. Effluents from factories contain numerous hazardous toxic pollutants, which have mutagenic properties, leading to carcinogenic disease through groundwater [7]. Contaminants may easily reach groundwater as a result of discharge to surface water bodies and subsequent infiltration down to the groundwater [8].

The current scheme of water cycle in Kazakhstan's industrial sector is presented in Figure 1. It is clearly seen that legislation regulates all water use processes. Despite this, the problem of environmental pollution exists due to refinery activities. This study aimed at investigating a situation in the sphere of water use by the oil refinery industry in Kazakhstan.

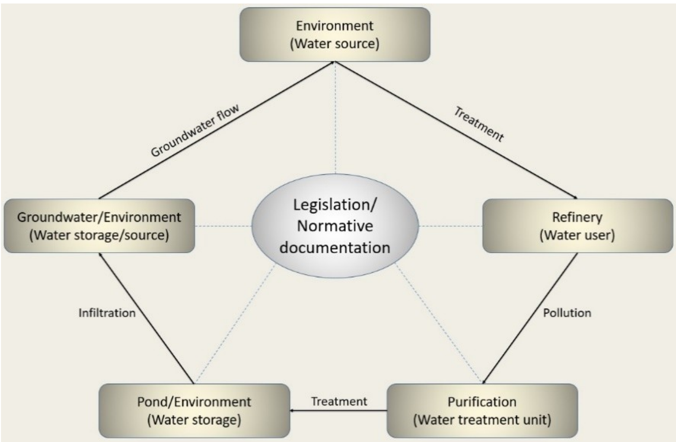

Figure 1. The existing framework for water use in oil refineries in Kazakhstan.

Thus, the study had the following objectives:

(a) Overview and compare national and international regulations in the case of water use, treatment and discharge.
(b) Investigate advanced wastewater treatment techniques as well as methods of rational water use.
(c) Assess the efficiency of wastewater treatment processes at the oil refinery factories in Kazakhstan and evaluate their influence on the environment in accordance with national and international safe water guidelines.
(d) Investigate experiences of other refineries reported in the literature concerning their implementation of tougher legislation and advanced water use methods.
(e) Suggest recommendations about possible ways to enhance each step of legislative control functions to prevent pollution and thus protect the environment and public health.

2. Materials and Methods

2.1. International and National Regulations on Water Quality

2.1.1. World Health Organization

World Health Organization (WHO) is the main international office of public health and water quality. They are responsible for preventing waterborne diseases around the world. Their goal is twofold: On the one hand, they recommend suitable health care regulations to governments, which is based on a scientific approach. On the other hand, they suggest general principles of effective risk management to householders and water suppliers. WHO produces a number of water quality guidelines, including on drinking-water quality, safe use of wastewater and safe recreational water environments [9]. The authors focused on two main documents that present solutions to identify and prevent risks before water is contaminated.

The main document is the "Guidelines for Drinking-Water Quality" (GDWQ). The primary purpose of the GDWQ is the protection of public health. The guidelines should ensure the safety of drinking-water supplies through recommendations for controlling hazardous constituents in water, such as waste from agriculture, transport, industry, etc. National or regional standards should be developed from the scientific basis provided in the GDWQ. The guidelines describe reasonable minimum requirements of safe practice to protect the health of water consumers. Usually, legislative and regulatory frameworks adapt the guidelines to address local requirements and circumstances.

According to the guidelines, Chapter 8.5.2 entitled "Chemicals from industrial sources and human dwellings" [10], chemical substances from industry can reach drinking water directly from discharge systems. Another way of contamination is infiltration of materials and products through the soil. In some cases, unsuitable handling and removal of industrial wastewater may lead to groundwater pollution. The high-priority approach to prevent this pollution is to use the encouraged good treatment practices.

Moreover, there is another document from WHO on "Safe use of wastewater, excreta and greywater". The aim of this document is, firstly, to provide public health care and, secondly, to regulate the rational use of wastewater and excreta in agriculture and aquaculture. The guideline states that "in many developing countries, wastewater treatment is not a feasible option, and non-treatment approaches need to be considered to prevent transmission of pathogens or exposure to hazardous chemicals. This is more demanding on regulators, as the measures entailed vary in time and space" [11].

2.1.2. European Union

The following three directives are main documents about providing safe water to consumers and water environment protection in the European Union (EU): The Drinking Water Directive (98/83/EC), The Directive Concerning Urban Wastewater Treatment (91/271/EEC) and Industrial Emissions Directive (2010/75/EU). EU states that protection of the environment is based on the precautionary principle. It includes, firstly, priority treatment preventive actions and, secondly, the compulsory rule that the polluter should pay. According to the Directive Concerning Urban Wastewater Treatment [12], the process for treatment can be very expensive. Therefore, enterprises must provide development of innovative water treatment technologies to achieve safe water.

The objective of the EU Urban Wastewater Directive is to protect the environment from negative effects from urban and industrial wastewater discharges. The Directive, in Section C, Annex 1, states that industrial wastewater must be subject to such pre-treatment. This requirement ensures the environment from adverse effect of discharges from the treatment plants and prevents receiving polluted water. In accordance with other Community Directives, wastes must be safely recycled in an environmentally acceptable manner [13]. The industrial wastewater that flows to sewage systems should be subject to general regulations of treatment similar to that of urban wastewater, whereas discharges from certain industrial sectors of biodegradable industrial wastewater should be subject to suitable regulations before entering the recipients.

2.1.3. Kazakhstan

Legislation in the sphere of water resources use is regulated by four documents: (1) the "Law on the Protection of the Environment of the Republic of Kazakhstan"; (2) the "Water Code of the Republic of Kazakhstan"; (3) Order No. 209 of the Minister of National Economy of the Republic of Kazakhstan dated 16 March 2015, "Sanitary and Epidemiological Requirements for Water Sources, water intake points for household and drinking purposes, domestic and drinking water supply and places of cultural and domestic water use and water safety" with the generalized list of maximum permissible concentrations and approximately safe levels of exposure for harmful substances for water; and (4) Order No. 110 of the Minister of Environmental Protection of the Republic of Kazakhstan dated 16 April 2012 "On Approval of the Methodology for Determining norms of emissions into the environment" [14,15].

The method for calculating the maximum permissible discharges (MPD) of substances discharged from the wastewater of enterprises into storage tanks was developed for the industry. This technique contains a system of mathematical equations that allow calculating maximum concentration of pollutants for different types of wastewater. This water is discharged into special natural or artificial water storage facilities. The calculation algorithm considers the natural, climatic and hydrogeological conditions of the recipient. It also pays attention to background characteristics. According to the methodology, effluents may contain pollutants if the concentrations do not exceed the already existing concentration in the recipient [15].

2.2. Description of the Area and the Industry

Kazakhstan's refining sector is represented by three large oil refining enterprises. The plants were built during the Soviet Union period in different parts of the country. These factories are presented in Table 1 and Figure 2.

Figure 2. The locations of refinery plants in Kazakhstan.

Table 1. Oil refining volumes in Kazakhstan's refineries in 2016 [16].

Name	Oil Refining Volumes, Million Tons per Year	Oil Refining Capacity, Million Tons per Year	Processing Depth (Conversion Ratio), %
"Atyrau Refinery" (AR)	4.491	5.0	65.2
"PetroKazakhstan Oil Products" (PKOP)	4.272	5.3	75.4
"Pavlodar PC Plant" (PPCP)	4.036	5.1	76.6

Modern Kazakhstani refineries are sophisticated complexes for separating and modifying crude oil into different products. The general scheme is presented in Figure 3. The main objective is production of fuel, residual fuel oils, lubricants and many other petrochemical and chemical products. The initial refinery configuration was the topping refinery, which was designed to distil crude oil into a limited range and yield of products. It was composed of different units such as tankage, atmospheric and vacuum distillation units, recovery facilities for gases and light hydrocarbons, and the necessary utility systems such as steam, power, and water-treatment plants. The addition of hydrotreating and reforming units to this basic configuration resulted in a more efficient hydroskimming refinery, which produced desulfurized distillate fuels and high-octane gasoline. At the same time, refineries processed up to half of incoming crude oil. During the last 30 years all three refineries were modernized. Initially, a gas–oil conversion plant and a catalytic cracking unit were added. In the last five years, an olefin conversion plant, a polymerization unit and coke calcination units were implemented in the existing scheme of plants. The changes allow enterprises to increase processing depth and thereby produce large outputs of gasoline with the remainder of their products distributed among liquefied petroleum gas, jet fuel, diesel fuel and a small quantity of coke. Additionally, refineries also supply different substances, such as propylene, benzene, toluene, xylenes, etc., for further processing into polymers [17–19].

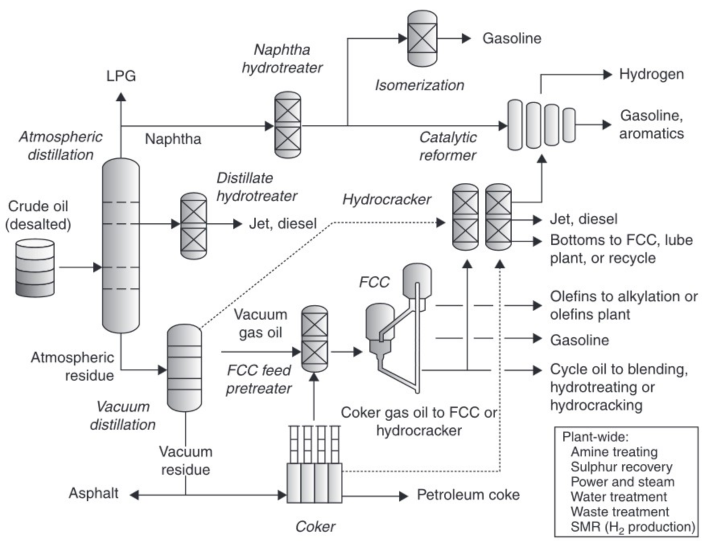

Figure 3. General scheme of an oil refinery plant [20]. LPG, Liquefied Petroleum Gas; FCC, Fluid Catalytic Cracking Unit.

2.3. Use of Water for Technological Purposes

The water supply system of an oil refinery is a whole complex of several different sub-systems. The scheme depends on the technological units' purpose and the quality of the incoming water as well as the composition of the generated wastewater. The amount of water consumed by the process units depends on the specific technology of the oil processing or crude oil fractions [21,22].

The supplied water must be suitable for production needs and satisfy the requirements by qualitative characteristics. Usually, water is received from available open sources or from the drinking water pipelines. These types of water can be easily adapted to appropriate quality. The incoming water quality indicators often exceed the permissible values, e.g., turbidity, suspended solids, iron, manganese, etc. Thus, pre-cleaning is needed to produce an adequate water quality. In Kazakhstan, factories obtain water for technical processes from the large rivers: Irtysh River (PPCP), Ural River (AR) and Badam River (a tributary of Arys River, PKOP).

The oil refining process starts in the atmospheric and vacuum distillation units. Those units are associated with the consumption of several by-products and reagents, including water, which is used for various purposes, for instance as a cooler of process units and equipment, and a cooling agent of the final product. Water is also used as a solvent for the preparation of reagent solutions as well as a source of steam or condensate. Furthermore, other reagents are added during a technological process, such as demulsifiers for dehydration of oil, ammonia to neutralize organic acids and sulfur compounds for treatment of light distillates.

There are three main sources of wastewater contamination at the refinery: (1) recycling of sulfurous oil and treatment of petroleum products with alkalines, which gives highly concentrated sulfurous alkaline wastewater; (2) complex processing of oil and gas to produce synthetic products generates wastewater with organic acids, alcohols, phenols, etc.; and (3) processes of desalination and dehydration. In the final source, wastewater contains demulsifiers and sulfonaphthones. All these substances are sources of harmful production, which leads to environmental pollution [23–26].

It is necessary to emphasize the harmfulness of some chemicals. Oily wastewater consists of hundreds of organic and inorganic compounds, some of which severely jeopardize the environment. Effluents include aromatic hydrocarbons, which have high toxicity and a stable structure. These include polycyclic aromatic hydrocarbons (PAH), which affect both the environment and human health. Carcinogenic, teratogenic and mutagenic properties were investigated and presented by different authors [27]. Degradation of PAH is a very difficult process, which leads to their high persistence in the environment. Another group of hydrocarbons in contaminated water is BTEX (benzene, toluene, ethylbenzene and xylenes). High concentration of those compounds can be rapidly absorbed by the human body. They can lead to damage of the brain and nervous system, rapid heart rate, dizziness and unconsciousness. The long time effect of consumption of even low concentrations may cause cancer [28]. Phenols are considered very hazardous for human health [29]. Heavy metals such as chromium, iron, nickel, copper, molybdenum, selenium, vanadium and zinc can also be found in wastewater from oil refineries [30].

2.4. Wastewater Treatment Technology Review

In an oil refinery, wastewater treatment cleans processed water, stormwater, and sewage. Contaminated water flows from every technological unit. Water can be polluted in the facilities that produce wash water, condensate, liquids from stripping unit, and caustic and neutralization acids. The wastewater contains suspended solids, dissolved salts, oil and grease, nitrogen compounds, organic sulfides, and other substances [26].

Conventional treatment schemes include broad variations for each step of treatment: pre-treatment, primary, tertiary (secondary) and post-treatment. The following reviews and investigations show innovative ways to enhance each part of the whole process. Figure 4 presents the conventional scheme of wastewater treatment unit at refinery enterprises.

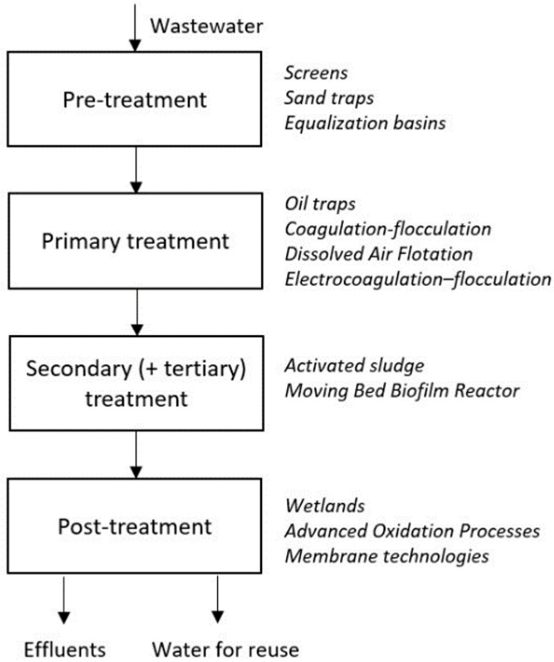

Figure 4. General scheme of wastewater treatment processes at oil refineries.

2.4.1. Primary Treatment

Settling ponds are used as a first step in the treatment process. Here, a majority of suspended solids are separated from the wastewater under the action of gravity and settle on the bottom. Oil and grease are floated on the surface and removed with the sludge. Heat is supplied to accelerate the removal of insoluble heavy oily emulsions. After that, precipitation of different chemicals is used for removing dissolved solids. Wastewater with high concentration of acids is treated by ammonia, lime, or sodium carbonate. Alkaline wastewater is treated with acids (usually sulfuric or hydrochloric), or carbon dioxide gas. Sometimes additional treatment of suspended solids is needed. Precipitation of flocculation agents (aluminum or iron salts) is used to agglomerate small particles and make them heavier or lighter, depending on the treatment method: sedimentation, filtration or air flotation. Soluble organic matters are removed with activated sludge digests. It is possible to decompose sulfides and ammonia by vaporization. Soluble hydrocarbons and their derivatives, especially phenols, are removed by solvents.

To enhance the efficiency of this step, Santo et al. [31] suggested using dissolved air flotation (DAF). This method was first used in the oil refinery industry in Egypt [32,33]. Spraying air into water or bubbling air through the water removes remaining traces of volatile chemicals such as petroleum hydrocarbons and ammonia. Significant removal of total organic carbon (TOC), chemical oxygen demand (COD) and turbidity was achieved. Advantages of this application are easy operation and low space requirement.

In addition, electrocoagulation–flocculation has been combined with the traditional method for primary treatment. Several different industries have successfully applied this method [34–37]. As a result of electrolysis, charged particles are neutralized in raw wastewater and subsequently form flocs. It is possible to remove phenol, anions such as nitrate and nitrite, cations such as ammonia, and metals as well as COD, TOC, color and turbidity [35,38–42]. This method has been implemented for a pilot project at Shazand Oil Refinery in Arak, Iran [43]. This method is recommended as a high-speed, non-expensive and environmentally friendly.

2.4.2. Secondary (Tertiary) Treatment

Some reviews describe tertiary treatment methods [26,44,45]. Traditional activated sludge system with aerobic and anaerobic zones are usually enhanced by different applications. One common application is MBBR (Moving Bed Biofilm Reactor). An aeration tank is filled with wastewater after pretreatment and consists of special plastic carriers with growing bacteria on their surface. The biodegradation process is resistant to toxic and shock loads. Drawbacks of this method are hard to operate a process and high cost. In addition, high energy requirement and production of polluted sludge may affect to the environment. However, this method shows high efficiency for removal COD, TOC and nitrogen compounds. Several scientists reported about using this method at petroleum refineries in Sweden, USA and India [46–48].

2.4.3. Post-Treatment

Additional treatment removes specific pollutants, including salinity, organic matters, BTEX and other partially soluble hydrocarbons, such as PAH. Recently, sustainable schemes of wastewater treatment also implement a post-treatment step, including membrane technologies, advanced oxidation processes and wetlands [18,26,49–53].

Munirasu et al. [54], Alzahrani et al. [55] and Gong et al. [56] presented detailed reviews of the use of membrane technology. Depending on pore size, different membrane technologies are defined: microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO). Different methods are chosen for specific demands of raw water quality and output water requirements. The authors of [57–60] showed the effectiveness of these process for oily wastewater, even at large industrial scale. On the other hand, high amounts of contaminants clog the membrane, which leads to high cleaning cost for constantly changing them. A refinery could use this method if potential benefits from implementation are higher than expenditure.

Advanced oxidation processes (AOP) are suggested to solve the problem of removing hard-degradable organic matters. Hydroxyl radical (•OH) is produced to provide a high oxidation potential, which destroys organic molecules in wastewater [61]. To initialize this reaction, ultrasound, ozonation, photocatalysis and peroxide oxidation are used [62–65]. One of the most popular AOP methods is Fenton's reaction, based on using Fe^{2+} in an acidic aqueous environment to produce hydroxyl radical [66–68]. Recently, this treatment method has been enhanced by different authors to overcome existing disadvantages: the pH dependency and temperature variability [69–72].

Finally, probably the most famous post-treatment method is wetland use. Currently, oil refinery countries use wetlands for wastewater post-treatment. Previously, wetlands were constructed only for domestic water treatment. Therefore, for the last 20 years, wetlands have been applied to industrial wastewater treatment [73]. There are many examples and many reviews of successful application of wetlands for oil refinery wastewater treatment [74–83]. However, certain climatic conditions are required to sustain the wetland systems, e.g., Wang, et al. [84] showed that wetlands do not function well during the cold season.

2.4.4. Wastewater Reuse

Application of advanced treatment methods assumes that treated wastewater has to be reused. Different variations of water saving techniques are proposed for refinery enterprises in Brazil [85,86], Iran [87,88], Netherlands [89], Mexico [90], USA [91], Romania [92], China [93] and Australia [85]. There are two main approaches, which should be combined: modeling of sufficient water network allocation and suitable treatment methods for each case.

Historically, El-Halwagi and Manousiouthakis [94] were the first to analyze systems of mass exchange network in the industry. Later, Wang and Smith [95] described a detailed system of optimization water use in some specific cases using graphical method. This technique includes measurement of wastewater flow generation, water consumption index and contaminants mass transfer within the industrial processes. It allowed only minimizing wastewater flow generation. Later, Mann and Liu [96] proposed that, in some cases, it is possible to establish regeneration units before wastewater treatment step and supply regenerated water again to the process. Bagajewicz et al. proposed modeling investigations for the implementation of water reuse system towards zero discharge policy [97,98]. Alva-Argaez presented conceptual work about cost and optimization efficiency for oil refineries [23]. Finally, an appropriate treatment method has to be suggested for each case. After treatment, recycled water can be reused again as a process water for every unit inside the factory.

2.5. Wastewater Treatment Technology in Kazakhstani Refineries

All factories in Kazakhstan use the same wastewater treatment systems, consisting of on-site mechanical (as a primary step) and biological (as a secondary step) treatment. It should be noted that the biological treatment systems of PPCP and PKOP were built during the Soviet Union period and now are in urgent need of modernization. Moreover, there is a significant time gap between when the plants started to operate and the implementation of the biological treatment: PPCP started production 1978, while the biological treatment facilities were built in 1981; and AR started its production in 1945, while the biological wastewater treatment plant was not built until 2006.

The existing scheme in Kazakhstani factories includes two unrelated systems, divided by the content of the contaminants. The first system is represented by conditionally "neutral" effluents contaminated with oil products and mechanical impurities from the primary processing unit, deep processing oil complex, hydrogen production plant, sulfur production plant, bitumen production plant, washing and steaming station, commodity-raw parks, and stormwater from the territory of the plant. This water is considered conditionally clean, and after treatment is reused in the cooling towers. The second system includes wastewater from effluents of desalination and dehydration units, sulfurous alkaline wastes from the blocks of alkalization, drainage from the pits, discharges after flushing from the loading piers, wastewater after flushing and steaming station, and process condensate. After treatment, this water is fed to the evaporation storage tank. Both waters pass through the same steps of treatment but in parallel processes [99].

The technology of wastewater treatment at PPCP is presented as an example of the treatment facilities in Kazakhstani plants in Figure 5.

Mechanical wastewater treatment is designed to separate undissolved mineral and organic impurities by the method of settling wastewater. Initially, wastewater flows through the sand trap for filtration. Oil floats to the surface of water and is separated by the oil separating trap. At the same time, the concentrations of pollutants in wastewater is reduced to a value where it is possible to perform physical and chemical treatment in the radial settling basins and flotators. Physicochemical treatment is intended to remove fine and colloidal particles of petroleum products and mechanical impurities from the wastewater. The coagulant (aluminiumsulfate) is added to the wastewater. It produces and strengthens aggregates of particles of the colloidal system. These adhering aggregates of contaminants are removed in the flotators when air bubbles and wastewater are separated into phases. The wastewater, treated by physicochemical method, is supplied to the biological treatment facilities for further treatment.

The biological treatment facilities include three parts: (1) aerotanks, where wastewater is continuously mixed with an activated sludge and aerated until oxygen saturates the air; (2) radial sedimentation tanks are intended to separate the sludge mixture into clarified water and activated sludge; and (3) the bioproducts are intended for post-treatment of wastewater of the second system.

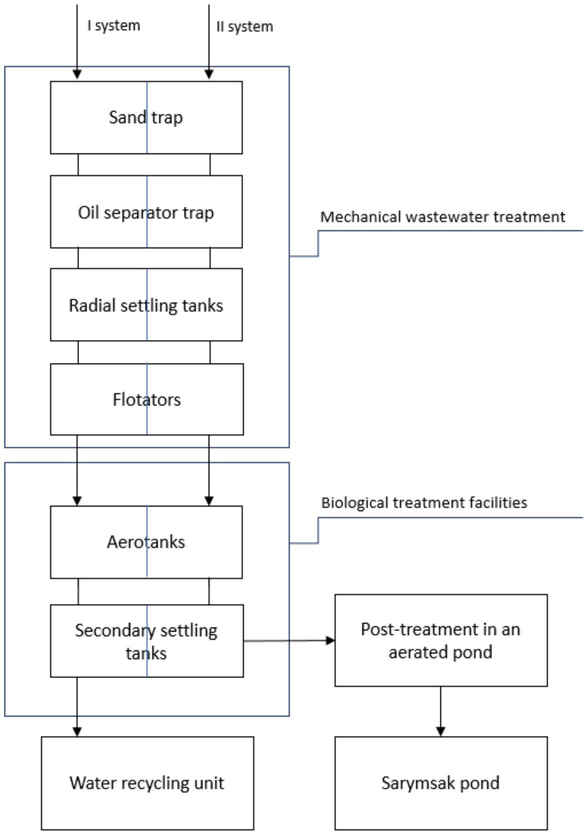

Figure 5. The block diagram of wastewater treatment processes at PPCP.

The operation principle of the biological wastewater treatment plants is based on the oxidation of organic pollutants due to activity of microorganisms in active silt under intensive aeration. Active sludge adsorbs and oxygenates a significant part of the contaminants. Organic substances in wastewater (organic acids, alcohols, proteins, carbohydrates, etc.) feed microorganisms in an active sludge. The microorganisms obtain the nitrogen, phosphorus and potassium necessary for life from various compounds: nitrogen from ammonia, nitrates, and amino acids; and phosphorus and potassium from mineral salts. One part of pollutants is oxidized by microorganisms. After that, it is used in biosynthesis processes (formation of the active sludge biomass). The other part is converted into other oxidation products: water, carbon dioxide, nitrate-sulfate ions, etc. [100].

2.6. Final Discharge of Treated Wastewater

There is a different approach to the final disposal of treated wastewater at all three Kazakhstani plants.

AR sends effluent after the biological treatment through a channel to the existing natural evaporation pond, located 3 km from the plant. The channel starts at the plant, runs along the southeastern border of the city and ends in an unprotected evaporation pond. The area of the pond is 10 km^2. It is located 1.5 km southeast of the city boundary and 10 km from the Caspian Sea.

In PKOP, the wastewater after treatment and mixing with drinking water is discharged into the Akdalinsky evaporation pond, located 96 km from the plant through the buffer channels. Buffer channels are open reservoirs formed by excavation of the soil, which is covered with reinforced concrete with waterproofing. This pond is connected with the Arys River, the main water source for agriculture fields in the south part of Kazakhstan.

PPCP uses a pipeline to deliver effluents to Sarymsak pond. This storage area, originally a natural salt lake, is used for receiving, storing, mineralizing and unloading biologically treated wastewater from PPCP. There are no water intakes, recreation and bathing areas, or agriculture near its location. The pond is located 14 km to the northwest of the plant and covers an area of 606.1 ha. There are two villages around the pond: Berezovka village in 2.5 km to the north and Michurino village in 8 km to the northwest. The main water source in Kazakhstan—Irtysh River—is located 9 km to the west from the pond.

3. Results and Discussion

The data employed include gathered documentation and lab results from three oil refinery companies. Enterprises were denoted as "X", "Y" and "Z", to protect their confidence and use available data only for scientific purposes. Data from Refinery "X" were used as an example to show a system of wastewater management at Kazakhstani enterprises.

Discharge limits for each oil refinery were established separately between the plant and the government. This allows the factory to determine the quality parameters of wastewater (Table 2). When the permissible concentrations of pollutants in discharging wastewater were established, calculation approach was based on the following two facts: (1) projected and actual purposes of the recipient—reception and accumulation of wastewater from the plant—which means that pond is not used as a source of water for agricultural and domestic purposes; and (2) it is possible to discharge polluted wastewater with existing concentrations of different contaminants, if those concentrations do not exceed the permissible values in the pond. The reason for the already high concentrations of pollutants in the recipient is a result of a time difference between the start of contaminated water discharge by the factories and start of the work of treatment units.

Table 2. Maximally permitted concentrations of different parameters in effluent of three Kazakhstan oil refineries [100–102].

Parameter	Units	Refinery X	Refinery Y	Refinery Z
Ammonia (NH_4^+)	mg/L	55.18	8.0	4.53
Total petroleum hydrocarbons (TPH)	mg/L	3.02	8.0	2.03
Biochemical consumption of Oxygen (BOD)	mgO_2/L	17.82	16.6	11.6
Nitrates (NO_3^-)	mg/L	19.2	7.8	8.96
Nitrites (NO_2^-)	mg/L	7.7	0.5	-
Sulfates (SO_4^{2-})	mg/L	643.05	500.0	471.1
Phenol's index	mg/L	0.25	0.05	0.182
Chlorides (Cl^-)	mg/L	169.8	350.0	678.8
Suspended solids	mg/L	20.98	25.75	6.05
Surfactants	mg/L	0.52	2.80	1.27
Phosphates (PO_4^{3-})	mg/L	1.05	2.0	6.89
Total Dissolved Solids (TDS)	mg/L	Existing concentration	6000	-

"-": not controlled.

Table 3 presents the characteristics of wastewater effluents discharged from Refinery X during the period between 2014 and 2017. Measurements were provided twice a day, every day and analyzed in the lab of the factory. Factory discharges the wastewater with the ammonia concentration approximately 50 mg/L, while the normal concentration of ammonia for municipal effluents is equal to no more than 2.0 mg/L. The same situation is found for TPH. The concentration of TPH in effluents is about 1.2 mg/L, when the limit for the concentration in treated municipal wastewater is 0.1 mg/L.

The concentration of BOD is about 10.6 mgO_2/L, when allowed concentration for safe water is no more 3.0 mgO_2/L.

Table 3. Concentrations of different parameters in effluent of Refinery X.

Parameter	Units	Range	Median	Mean	Std. Deviation
Chlorides (Cl^-)	mg/L	49.80–135.04	70.61	82.48	26.47
Nitrites (NO_2^-)	mg/L	0.08–4.37	0.43	0.10	1.27
Sulfates (SO_4^{2-})	mg/L	238.32–588.73	469.50	449.04	90.98
Nitrates (NO_3^-)	mg/L	1.77–16.41	13.23	12.49	3.96
Ammonia (NH_4^+)	mg/L	38.56–54.34	52.36	49.26	5.97
Total Petroleum Hydrocarbons (TPH)	mg/L	0.68–2.15	1.23	1.30	0.40
Phenol's index	mg/L	0.01–0.03	0.02	0.02	0.01
Suspended solids	mg/L	4.40–9.10	7.69	7.29	1.35
Surfactants	mg/L	0.20–0.45	0.36	0.34	0.08
Biochemical oxygen demand (BOD)	mgO_2/L	8.51–13.12	10.56	10.60	1.48

As a result, enterprises cause significant damage to the environment. This is reflected in an infiltration of pollutants into the groundwater. According Kazakhstani Sanitary and epidemiological requirements for water sources, groundwater could be used for non-centralized drinking water supply; this is especially relevant because about half the rural population uses decentralized water sources and about 40% of population live in rural areas in Kazakhstan [103,104]. Thus, the government established this standard for groundwater quality in observation wells to eliminate risk of groundwater pollution and prevent public health hazards. Concentrations of hazardous material are established the same way as for drinking water [105]. Some chemical parameters are exceeded in the observed wells' samples around the wastewater receiver pond of Refinery X (Table 4). This situation leads to potential threat of human health. In total, 35 samples from 9 wells were collected and analyzed between 2015 and 2016, during both the rainy and the dry season.

Table 4. Descriptive statistics of groundwater quality * from observed wells around the water facility storage area of Refinery X.

Parameter	Units	KZ, WHO Standards [10,105]	Range	Mean	Std. Deviation
Chlorides (Cl^-)	mg/L	350.0	15.00–16,000.00	2201.33	4344.54
Sulfates (SO_4^{2-})	mg/L	500.0	152.71–9400.00	1366.97	2720.60
Total Petroleum Hydrocarbons (TPH)	mg/L	0.1	0.11–0.75	0.33	0.18
Total Hardness (TH)	mmol/L	7.0	3.65–377.50	41.86	92.19
Sodium (Na^+)	mg/L	200.0	10.00–7900.00	1159.43	2099.72
Potassium	mg/L	12.0	0.00–34.00	3.30	7.49
Total dissolved solids (TDS)	mg/L	1000	1041.00–36,392.00	5458.37	9903.54
Nitrites (NO_2^-)	mg/L	3.0	0.00–14.50	0.62	2.45
Nitrates (NO_3^-)	mg/L	45.0	0.30–21.00	3.96	5.30
Ammonia (NH_4^+)	mg/L	2.0	0.00–10.91	1.83	3.11
Carbonates (CO_3^{2-})	mg/L	-	0.00–72.60	19.05	14.89
Hydrocarbonates (HCO_3^-)	mg/L	-	44.50–709.43	362.28	154.32
Calcium (Ca^{2+})	mg/L	-	8.60–2700.00	126.19	455.10
Magnesium (Mg^{2+})	mg/L	-	28.00–3600.00	436.19	891.50
Surfactants	mg/L	0.5	0.00–1.44	0.36	0.36
pH	pH units	6–9	7.88–9.00	8.55	0.33
Free carbon dioxide (CO_2)	mg/L	-	0.00–19.16	1.34	3.75
Phenol's index	mg/L	0.25	0.00–0.12	0.01	0.02
Phosphates (PO_4^{3-})	mg/L	3.5	0.01–0.19	0.03	0.03

"-": not controlled; *: standards for drinking water when groundwater can be used for drinking purposes.

High concentrations of TPH, TDS, TH, chlorides, sulfates, sodium and potassium were detected in the observed wells around the water storage facilities. There were high concentrations of TPH and TDS in all wells, which exceeded KZ- and WHO-recommended limits for these substances.

Some studies show that consumption of water with TPH may lead to carcinogenic disease by the reason of inherent toxicity [30,106,107]. The TH in the groundwater samples varied between 3.65 and 377.50 mmol/L. Based on the Todd classification, all groundwater samples could be classified as very hard [108]. The Cl^- concentrations were between 15.0 and 16,000 mg/L, with most groundwater samples exceeding WHO's 350 mg/L permissible limit. In addition, SO_4^{2-} concentrations exceeded the limit by 19 times. There is a possible health-related concerns regarding K^+ and Na^+ content in the groundwater because concentrations in wells was over permissible WHO and KZ limits. Finally, randomly exceeding concentrations of surfactants, NO_2^-, NO_3^-, and NH_4^+ were identified. Consumers normally would reject this type of contaminated water for drinking purpose in accordance of WHO recommendations [10].

More attention has to be paid to the fact that none of the factories provide control of heavy metal and toxic hydrocarbons in their effluents and monitoring wells.

4. Summary

Industrial effluents are potentially very harmful. They can reach groundwater and create serious damage to public health through consumption of polluted water. To be a part of global society, huge water users must follow sustainable management of water and sanitation [109]. Industry faces the challenge of rational use water by efficient wastewater treatment management.

This review shows that there are two ways to modify situation: (1) introducing efficient and innovative water use and treatment techniques; and (2) improving legislation.

Since the 1980s, some surveys and investigations have tried to find the relationship between legislation and industrial emissions to the air and water. A clear correlation between these parameters has been found. In Japan, in 1980, the impact of legislation for improvement effluent water quality was described [110]. Industry supplied their wastewater to municipal sewerage system. Government obligated the industry to install pretreatment facilities for prevention of low-quality water. Spot inspections, administrative fees and toughening of legislation led to discharge water with restricted requirements. Hamer [111] discussed the wrong opinion to respect and allow pollution of receiving water. He examined interactions among Swiss, Dutch and British legislations and industry and environment. Swiss legislation aimed to stop water pollution by 1982. For this purpose, they established strict quality parameters for discharged water by federal law. Netherlands also provided governmental authority on the sphere of water pollution and followed "polluter pays" principle. The aim of Surface Water Pollution Act was accepted to eliminate contamination. Discharge fees were provided and grew progressively every year. It led industry to use the best treatment technology to remove all pollutants from wastewater. In Great Britain, over years of long discussions, government adopted Control of Pollution Act. The enactment of this law was gradual. Economic troubles, administrative obstacles and unfair enterprises impeded the process of changes. Nevertheless, Britain reached necessary discharge quality parameters. Compared with historical experience, current EU has produced tougher legislation. This was proven by Wake [30]. She stated a reduction of total discharge in Europe for the last 40 years as well as declining rate of discharged chemicals, while the number of refineries that improved their treatment systems grew rapidly (from 23% to 91%) for 30 years. The United States Environmental Protection Agency (EPA) firstly in 1985 proposed special guideline for petroleum refining industry [112]. This standard stated one common rules for all enterprises and proposed new technologies, including pretreatment and advanced treatment, to achieve necessary limitations of pollutants. This document is revised constantly.

There also are some published examples of violence over effluent quality by refining enterprises. Osin et al. [113] showed that oil industry in Nigeria did not follow governmental standard of effluent quality. Whereas the law proposed and adopted Environmental Guidelines and Standards for the Petroleum Industry in Nigeria, it was not implemented. Exceedances of almost all key indicators were discovered. Bandyopadhyay reviewed the efficiency of law in India [114]. Constant violations of national standards were reported. The author also noted that the law did not cover all toxic pollutants that can be in water. He suggested revising the current standard and toughening it. Aljuboury et al. showed that petroleum wastewater exceeded the standard limit in Oman [115].

WHO's documents state that developing countries, including Kazakhstan, do not have appropriate legislation for wastewater treatment [10]. This has been confirmed by several investigations [116,117]. It is very important to note that GDWQ values for chemicals from industrial activities does not differ from the significance in drinking water. In addition, WHO declares that it is necessary to reduce water pollution [10]. Nevertheless, enterprises in Kazakhstan increase the amount of contaminants in wastewater. However, the WHO is only an advisory organization. It suggests governments adhere to its recommendations and cannot control them. At the same time, the Council of the European Communities produces and controls the suitable legislation on water use. For example, the EU Directive Concerning Urban Wastewater Treatment does not provide separate standards for the content of pollutants in treated wastewater for enterprises in EU. Rules and standards are established for everyone. In contrast, the modern Kazakhstani legislation gives the right for industry to set their parameters for MPD much higher than those recommended by WHO.

It is significant that the standards for technical water quality are stronger than for drinking water. For instance, the amount of total petroleum hydrocarbons (TPH) must be absent for process water. In contrast, the maximum concentration of the parameter in drinking water is 0.1 mg/L. The amount of total dissolved solids (TDS) is equal to 500 mg/L, whereas the standard for drinking water is 1000 mg/L. The total hardness (TH) value is 11.6 mg/L, whereas the standard for drinking water is 14 mg/L [118]. The refineries care about the quality of incoming water, but they do not care about the quality of discharges, as shown clearly with the example of Refinery X in Tables 2 and 3. This is the violence of water balance and there is no agreement on sustainable resources use [119]. The enterprises must supply water to the environment at the same quality as they have obtained it.

The ineffectiveness of the existing administrative regulation was confirmed by the widespread violation of sanitary standards. The estimation by environmental authorities for each plant is negotiated separately between the factory and the government. Thus, the industry has received a legal permit for environmental pollution.

5. Conclusions

Water contamination by the industry is the result of a non-sustainable approach. According Katko and Hukka [120], a structured approach based on sustained institutional framework leads to high quality water service production through efficient water service infrastructure. We conclude that:

(a) Enforcement of legislation allowed developed countries to eliminate risks for environment and public health. It was the first step towards sustainable water use. Pressure of stringent law and high fees stimulated industry to implement innovative and high-efficient techniques of water use.
(b) The literature review shows that developing countries are on the way to minimizing potential damage to the society and nature. The practice of sustainable water use and care about saving water sources inspired conventional industrial society to improve the current situation.
(c) There is insufficient driving force represented by suitable law in Kazakhstan to enhance an efficiency of wastewater treatment at oil refinery enterprises in Kazakhstan. Low penalties and disadvantages of current legislation allows the situation to remain unchanged.
(d) The authors of this paper consider that toughening of the legislation as well as the ensuing use of new technologies in wastewater treatment systems is the only effective way to prevent potential damage to the public health of people who use groundwater as drinking water.

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Paper II

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ORIGINAL PAPER

Assessment of groundwater safety surrounding contaminated water storage sites using multivariate statistical analysis and Heckman selection model: a case study of Kazakhstan

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Abstract Petrochemical enterprises in Kazakhstan discharge polluted wastewater into special recipients. Contaminants infiltrate through the soil into the groundwater, which potentially affects public health and environment safety. This paper presents the evaluation of a 7-year monitoring program from one of the factories and includes nineteen variables from nine wells during 2013–2019. Several multivariate statistical techniques were used to analyse the data: Pearson's correlation matrix, principal component analysis and cluster analysis. The analysis made it possible to specify the contribution of each contaminant to the overall pollution and to identify the most polluted sites. The results also show that concentrations of pollutants in groundwater exceeded both the World Health Organization and Kazakhstani standards for drinking water. For example, average exceedance for total petroleum hydrocarbons was 4 times, for total dissolved solids—5 times, for chlorides—9 times, for sodium—6 times, and total hardness was more than 6 times. It is concluded that host geology and effluents from the petrochemical industrial cluster influence the groundwater quality. Heckman two-step regression analysis was applied to assess the bias of completed analysis for each pollutant, especially to determine a contribution of toxic pollutants into total contamination. The study confirms a high loading of anthropogenic contamination to groundwater from the petrochemical industry coupled with natural geochemical processes.

Keyword Kazakhstan · Petrochemical industry · Water quality · Principal component analysis · Cluster analysis · Heckman selection model

Abbreviations

Alk	Alkalinity
BTEX	Benzene, toluene, ethylbenzene and xylenes
CA	Cluster analysis
EPA	United States Environmental Protection Agency
EU	European Union
GW	Groundwater
km	Kilometers
KZ	Kazakhstan
m	Meters

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PAH	Polycyclic aromatic hydrocarbons
PC	Principal component
PCA	Principal component analysis
TDS	Total dissolved solids
TH	Total hardness
TPH	Total petroleum hydrocarbons
UN	United Nations
WHO	World Health Organization

Introduction

Safe drinking water is one of the sustainable development goals announced by the UN; however, in many countries, the goal remains far off. In 2015, the distribution of global groundwater use was estimated to 50% for drinking purpose and 43% for irrigation (UNESCO 2015). Historically, groundwater quality has been deteriorated by human activities, such as agricultural, industrial, and urbanization processes (WHO 2006). In Kazakhstan, groundwater withdrawal amounted to 1.078 km^3 in 2016 (UN 2019). One crucial problem in the country is toxic wastewater from petrochemical factories (Radelyuk et al. 2019), a very important factor in Kazakhstani economy. The oil refinery industry is represented by three large factories, and their capacity is estimated to be 360 thousand barrels daily with an annual growth of 2.9% (BP 2018). Additionally, refineries are associated with petrochemical industry. Industrial clusters are established around core refineries. It leads to growth of production and increasing level of contamination. The problem is that the current methods of wastewater treatment in the petrochemical sector, as well as the conditions of the treatment units built during the Soviet era, do not assure a safe level of contaminants concentrations for the ecological systems. Thus, the existing discharge system has a significant negative impact on the environment and could potentially become a health issue for the population.

The groundwater is the main source for decentralized and centralized drinking water supply in rural areas in Kazakhstan, where more than half of the population live (Zhupankhan et al. 2018; Bekturganov et al. 2016). The perceived water quality has been assessed in several research and showed relative satisfaction (Tussupova et al. 2015, 2016). However, in situ water quality and potential risk for groundwater safety have not been covered within existing scientific literature. Simultaneously, petrochemical plants in Kazakhstan continue to discharge wastewater with high concentrations of different pollutants and these contaminants may reach the groundwater very easily. Despite of existing system of ecological monitoring, oil refinery cluster in Kazakhstan is ranked as one of the biggest sources of water contamination by United Nations Economic Commission for Europe (UNECE 2019). Recent studies showed that approximately 1.5% of total deaths in Kazakhstan caused by waterborne diseases related to water pollution, including industrial sources (Karatayev et al. 2017).

While contaminated sites occupy relatively small area, they belong to larger aquifers and potentially cause serious hazard (Maskooni et al. 2020). The contaminated sites are considered as a serious problem worldwide (Kovalick and Montgomery 2017). Moreover, the situation becomes worse if governments deny any environmental pollution or the contaminated sites are not investigated (Naseri Rad and Berndtsson 2019). Research-based approach can deal with the situations and helps do right decisions about remediation programs and protect population and environment from related risks (Naseri Rad et al. 2020). Thus, it is urgent to identify the main sources of groundwater pollution from petrochemical industry in Kazakhstan in order to eliminate the risks.

Multivariate statistical techniques have been widely used for assessment of surface and ground water quality (Shrestha and Kazama 2006; Naseh et al. 2018; Cloutier et al. 2008; Ghahremanzadeh et al. 2018; Noori et al. 2010; Patil et al. 2020). The natural transformations happen due to saltwater intrusion, lithological/geochemical processes, rainfall and snowmelt, eutrophication processes. The anthropogenic invasion due to urban development, industrial and agricultural activities, influence by rural settlements significantly contributes to groundwater pollution, and consequently, affects the water quality. Thus, multivariate statistical techniques are efficient tools identifying and separating the main probable sources of pollution in the context of land-use changes. Three techniques are particularly common: Pearson's correlation, Principal Component Analysis and Cluster Analysis. Correlation matrix is used to determine potential interactions between different chemicals by pairwise variables comparison. PCA is used to identify statistically the most significant parameters, which are considered as major contributors to total contamination. Finally, CA combines similar groups of observations together. The techniques have been successfully applied, e.g., Egbueri (2019) divided his study area in Nigeria into insignificantly and highly polluted sites by using CA. Awomeso et al. (2020) investigated and identified possible sources of groundwater contamination such as leachate from septic tanks, nutrients from agricultural fields and chlorine pollution. The multiple natural and anthropogenic sources of surface and groundwater pollution have been presented by Omo-Irabor et al. (2008) in Nigeria. Impact on shallow groundwater in irrigated areas has been investigated by Trabelsi and Zouari (2019) in Tunisia. Shrestha and Kazama (2007) combined sites as less polluted, medium polluted and highly polluted, based on the similarities of water quality indicators in Japan. The same was for Kazi et al. (2009) who investigated the problem of water contamination by agriculture and industry in Pakistan. Liu et al. (2003) showed influence of processes of saltwater intrusion and arsenic pollution in Taiwan. Groundwater pollution sources apportionment in a land with high density of agriculture, industry and urbanization has been investigated in southwestern China (Li et al. 2019). Hence, the multivariate statistical techniques let researchers successfully investigate certain case studies.

The aim of this paper is to analyse and interpret a dataset obtained during a 7-year (2013–2019) monitoring program of the wastewater discharge systems in one of the Kazakhstani industrial clusters. This dataset includes concentrations of substances in groundwater from nine observed wells surrounding the wastewater recipient. Kazakhstani law (Kazakhstan 2015) requires that strict standards for groundwater quality surrounding recipients are followed. If the requirements are neglected, the responsible company should take actions to eliminate the risks for the environment and people. Matrix correlation, PCA, and CA multivariate techniques were applied to (1) determine main pollutants with elevated concentrations in groundwater, (2) assess the contribution of each contaminant to temporal variations in groundwater quality and identify their potential origin, and (3) group the contamination sites affecting water quality and their potential sources by relevant similarities. The results contribute to the description of the spatial–temporal changes in groundwater quality of the study area. Heckman selection model was used to avoid bias of the results and look at specific properties of each pollutant more carefully. Moreover, the study highlights the main sources of contamination at the different locations of the study area and is thus of interest for local key stakeholders, groundwater modelling researchers, and risk analysis managers.

Materials and methods

Study area

The industrial site of this study belongs to the special economic zone and is located in the north-eastern part of Kazakhstan. The region is located in a sharply continental zone, where mean monthly temperatures range from − 19.3 °C in January to + 21.5 °C in July, with an annual mean of 3.5 °C, absolute maximum of + 42 °C and absolute minimum of − 47 °C. Annual precipitation is around 303–352 mm, including 264 mm in liquid phase. The driest months are May, June, and July. Potential annual evaporation is around 957 mm (Heaven et al. 2007). Average relative humidity equals 82% and 45% for the coldest and the hottest period of the year, respectively. 70–85 days of the year is represented with the humidity 80% and more.

The recipient pond (Fig. 1) is based on a natural bitter-salty pond for receiving and storing biologically treated wastewater from the nearby located petrochemical industry. According to Kazakhstani legislation (Kazakhstan 2012), this pond is not a source for drinking, domestic and irrigation water. The annual volume of received wastewater amounted to 1.63–2.21 million m^3 for the period 2009–2019, instead of designed 4.12 million m^3. The water volume and water surface for the same period are maintained within 3.6–6.7 million m^3 and 2.45–3.73 km^2, respectively, instead of the designed 23.5 million m^3 and 5.23 km^2, respectively. Observation wells are located out of barrier for groundwater quality monitoring and belong to permanent control from governmental bodies. The installation procedures followed appropriate installation technique in case of required installation materials and methods and planning of the location of the monitoring system (Houlihan and Lucia 1999). The depth of the wells

Fig. 1 Study Area. Green triangles show location of wells sampled

varies between 10.1 and 24.6 m below ground level. The groundwater depth in the wells varied between 1.1 and 4.9 m.

The hydrogeological conditions of the study area have been poorly investigated during soviet and post-soviet periods. The geological cross-section is represented by four geologic-genetic layers: contemporary sediments (land cover), upper-quarternary and contemporary aeolian–deluvial deposits (clayey sand) and upper-quarternary alluvial deposits (loam and/or fine to medium-grained sands). The geological profiles of the examined wells are presented in Fig. 2. Groundwater is represented by two aquifers: shallow unconfined and confined aquifers. The upper aquifer is composed of clay–sand and mixed size sands. The bottom of the aquifer lays on the depth 8.0–24.0 m below surface level. The aquifer is mainly recharged from water infiltration from the surface. The discharge is partly due to evapotranspiration and partly due to percolation to the underlying aquifer. Amplitude of seasonal fluctuation of groundwater table is about 0.7 m (Fig. 3). The figure shows that the GW level has peak values after the winter during the snowmelt season and after that reaches its minimal values during the summer. Interpolation using inverse distance method was used to establish GW flow direction and the bottom of the first aquifer. Figure 4 shows a contour map of the groundwater level and the elevation of the bottom of the unconfined aquifer. The second aquifer composed of medium-grained and small-grained sands. It is recharged from the head water and from the upper aquifer. The aquifer discharges to the nearest river, which is located 4 km west from the pond.

A total of 117 groundwater samples from the shallow aquifer were collected and analyzed between 2013 and 2019, from all observation wells. Sampling was made two times per year, in spring and autumn.

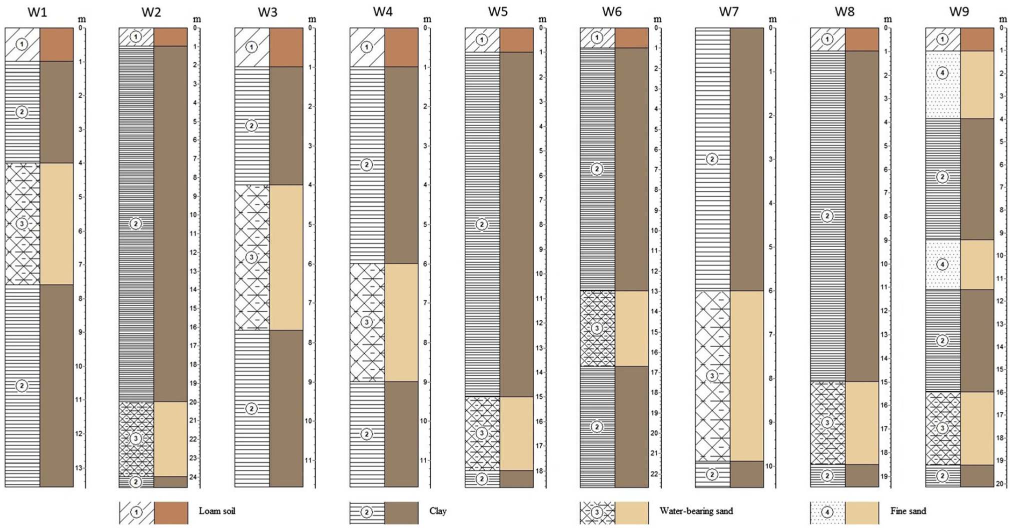

Fig. 2 Geological profiles of the examined wells

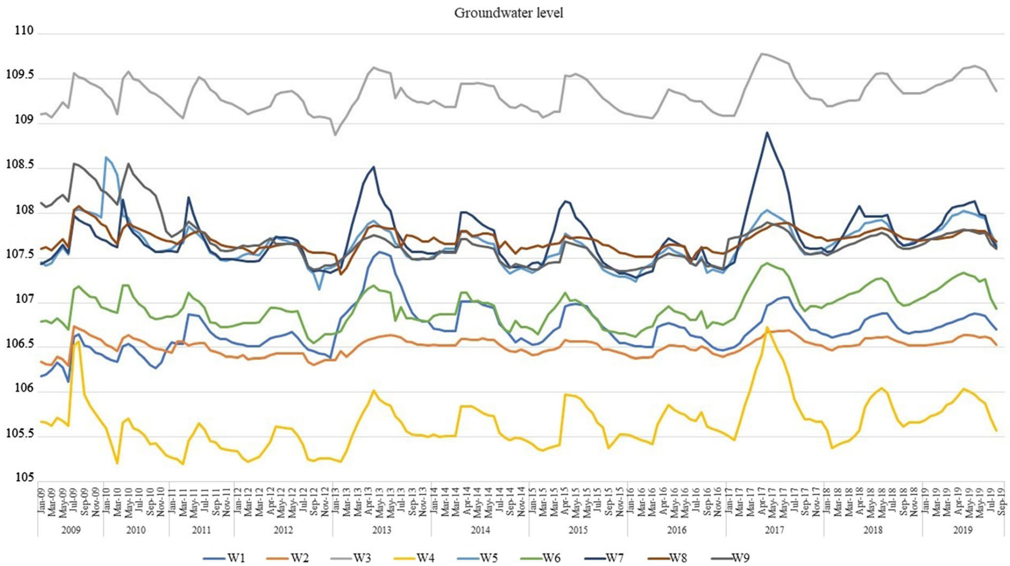

Fig. 3 Seasonal fluctuations of groundwater level in the nine wells

The groundwater depth was measured regularly from March to November each year. The procedures of the sampling and measurements are controlled by Kazakhstani legislation from the sufficient international standards (Houlihan and Lucia 1999). Before sampling, the groundwater in the well was evacuated several times (usually, three times) by pumping. The pumping equipment was also flushed prior to sampling

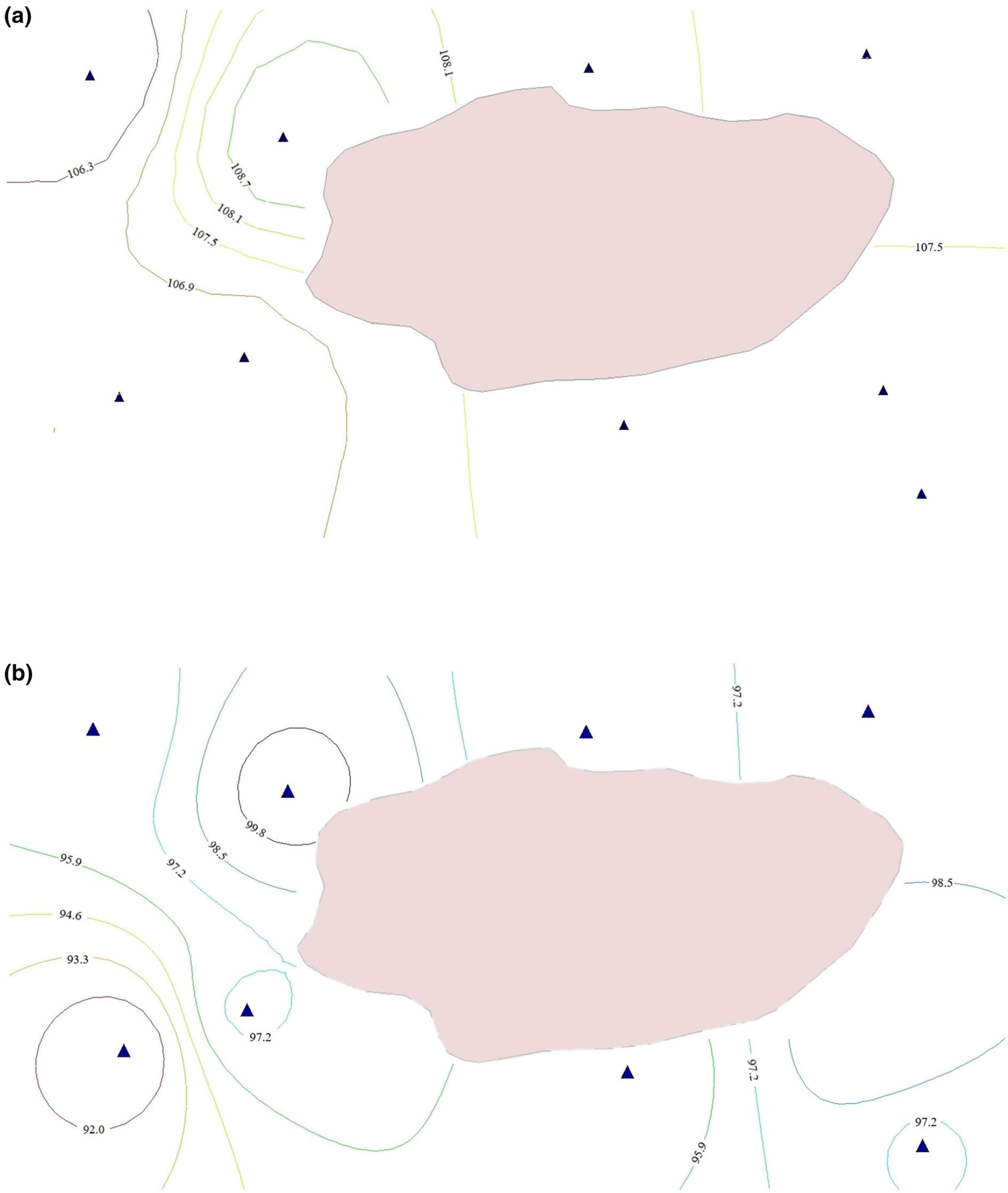

Fig. 4 **a** Contour map of groundwater levels on the study area, **b** Spatial distribution of the bottom of the first aquifer

to avoid unwanted pollution. After establishing a static water level, the sampler was immersed to a depth below the water table by 0.5 m or less. Water samples were collected in 1-l dark glass bottles. The vessels were moved into a transportable fridge for immediate delivery and analysis to the licensed factory laboratory. Extra samples were collected for the analysis of metals with acidification by HNO_3.

Multivariate statistical techniques

Correlation analysis, principal components analysis (factor analysis), and hierarchical cluster analysis were applied to identify the multivariate relationships between different variables and samples in the study area. The dataset was normalized for elimination of the effect from differences in units (Eq. 1).

$$Z_{ij} = \frac{(x_{ij} - m_i)}{\mathrm{SD}}, \quad (1)$$

where Z_{ij} are normalized values from x_{ij}, i is represented variables, j is the sample number, m_i is the mean value and SD is the standard deviation of the sample.

The relation between each pair of variables was measured by Pearson's correlation coefficient to determine the geochemical associations among different variables. Correlation coefficients greater than 0.5 were considered significant. PCA recognizes the most significant parameters from a big dataset of intercorrelated parameters and created independent variables (Eq. 2).

$$z_{ij} = a_{i1}x_{1j} + a_{i2}x_{2j} + \cdots + a_{im}x_{mj}, \quad (2)$$

where z is the component score, a is the component loading, x is the measured value of variable, i is the component number, j is the sample number and m is the total number of variables. Factor analysis (FA) is a similar technique as PCA. However, PC is presented as a linear combination of parameters. FA follows PCA and takes into account unobservable, hypothetical, and latent variables. They are included in equation with the special residual term (Eq. 3).

$$z_{ij} = a_{f1}f_{1j} + a_{f2}f_{2j} + \cdots + a_{fm}x_{mj} + e_{fi}, \quad (3)$$

where z is the measured variable, a is the factor loading, f is the factor score, e is the residual term according to errors or other source of variation, i is the sample number and m is the total number of factors.

Cluster analysis was used to assemble similar groups of observed wells due to similarities between their variables. Hierarchical agglomerative CA provided Ward's linkage distance, reported as D_{link}/D_{max}, which represents the quotient between the linkage distances for each case divided by maximal linkage distance. Produced dendrogram lets to analyse similarities easily. Ward's linkage, the Euclidean distance as similarity measurements, and Q-mode are usually used for cluster analysis for assessment of groundwater quality (Egbueri 2019; Cloutier et al. 2008; Kazi et al. 2009; Awomeso et al. 2020; Trabelsi and Zouari 2019; Amanah et al. 2019; Bouteraa et al. 2019).

Heckman selection analysis

Heckman selection analysis, to the authors' knowledge, has never been applied to assess the environmental characteristics. This type of analysis was adapted from the original work of Heckman in the economical science (Heckman 1979) and from the application this type of this method in other fields, for example in the assessment of energy production (Sun et al. 2014), urban transportation research (Kaplan et al. 2016) and estimating crash rate (Xu et al. 2017). The method in this study is used to assess unobservable variables, that potentially impact on the total contamination rate. Gadgil investigated the list of chemicals in the WHO guidelines (Gadgil 1998) and concluded that certain chemicals have no strong requirements for their concentrations in drinking water, as the exposure of exceeded concentrations for human health is not significant. The idea of this assessment is not just looking at several contaminants and their concentrations, but also to consider and evaluate other important factors such as location of the sampled value, percent of exceeding of the certain contaminant and individual characteristics of the contaminant. Selected variables were divided into two categories. First: chemicals seriously affecting health (rated as sanitary toxic due to Kazakhstani standard (Kazakhstan 2015)); second: other hazardous materials (rated as non-toxic). It is aimed to compare potential effect of toxic and non-toxic contaminants. We focused, on the one hand, on several pollutants with elevated concentrations, such as chlorides or sulfates, which are not rated as significant impact on health, but can be dangerous for other cases, for instance, for corrosion of pipes, or for irrigation properties of soil; on the other hand, on the contaminants, rated as dangerous for the health, or toxic (for example, hardness or petroleum hydrocarbons).

This model includes two-step equation, which is assumed as an advanced regression model equation:

$$Y_i = \beta_1 S_i + \beta_2 X_i + u_i, \quad (4)$$

where Y_i is considered as total contamination, S_i represents the concentration of chemicals, and X_i shows several contaminants as a set of control variables. The effect of the exceeded concentrations on the total contamination is given by the parameter β_1. Parameter i represents each individual observation.

Equation (4) does not consider other potentially important independent variables which can affect for final result. For example, it could be locations of the wells or individual characteristics of different contaminants such as their toxicity and exposure level in case of influence of chemicals for people's health. There could be a different input of high exceeding of non-toxic contaminant and low exceeding of toxic contaminant. Second one would be much more dangerous for health. Thus, more attention should be paid to the level of toxicity. Specific description of this equation can be written as:

$$\begin{aligned} &Y_i^* = \beta_1 S_i + \beta_2 X_i + u_i \\ &D_i = 1(\gamma_1 S_i + \gamma_2 Z_i + v_i > 0), \text{ and} \\ &Y_i = Y_i^* D_i, \end{aligned} \quad (5)$$

where (Y_i, D_i, S_i, X_i, Z_i) are observed random variables and 1(.) is an indicator function. The first equation represents the total contamination of all contaminants. The second equation is the selection equation, where D_i is added as a dummy variable indicating whether value i represents a measurement of toxic/non-toxic pollutant. A set of variables Z_i includes additional parameter such as a well value i. Set of control variables Z_i must include at least one variable which is not included in X_i (Sartori 2003).

All mathematical and statistical computations were performed using Microsoft Office Excel 2016, IBM SPSS Statistics 26 software and STATA 15.0 (StataCorp LP).

Results and discussion

Groundwater quality parameters

Table 1 presents the results of measurements of groundwater quality from the wells surrounding the recipient pond. Kazakhstani and WHO standards for drinking water were used for assessing all parameters. The concentrations of several parameters in wastewater, which are discharged into the recipient pond, are also presented in the table. Those characteristics came from the previous publication of the authors (Radelyuk et al. 2019).

As shown, all wells had exceeding concentrations of total petroleum hydrocarbons (see also Fig. 5). When the permissible concentration of TPH is 0.1 mg/L, the concentrations of TPH varied between 0.08 and 1.20 mg/L with mean value 0.42 mg/L, which exceeded the norm 4 times. Although low concentrations of TPH in water might be considered harmless, researchers found that long-term exposure to TPH causes carcinogenic diseases (Pinedo et al. 2013; Wake 2005). Table 1 also shows that dangerous concentrations of phenols were identified in all nine wells. This pollutant had been evaluated as very toxic and was included in the list of priority pollutants by Environmental protection agency (EPA 2012). The number of disorders has been discovered by acute exposure of phenol: muscular convulsions, hypothermia, muscle weakness and tremor, collapse, coma, etc. (Nair et al. 2008). There is a limitation in the assessment of the presence of phenol in our case study. However, the limit of the concentration of simple phenol (phenol index) is 0.25 mg/L according Kazakhstani standard. The same value is established in the standard of the factory for the observed wells (Radelyuk et al. 2019). At the same time, protocols of GW quality measurements name this parameter "volatile phenols". This type of phenolic compound is considered to be limited 0.001 mg/L. Thus, there is unclear situation of what limit should be used. Measured TDS values exceeded the KZ and WHO maximum permissible levels of 1000 mg/L in most cases on average five times (Fig. 5). Further, the total hardness in the groundwater samples ranged between 2 and 390 mmol/L with mean exceeding the standard six times (Fig. 5). According the Todd classification, almost all samples might be categorized as very hard water. Hard water may cause cerebrovascular and cardiovascular diseases (Stambuk-Giljanovic and Stambuk 2005). The chloride ion presence were between 56 and 24,757 mg/L, with most samples elevated WHO's 250 mg/L recommended limit (exceeding 9 times on average) (Fig. 5). There are possible health-related concerns regarding Na^+ content in the groundwater because the mean elevated concentrations in the wells were six times over the

Table 1 Water quality parameters for groundwater samples from the observed wells. All units are in mg/L, excluding pH (pH unit) and total hardness (mmol/L)

Parameters	WHO limits* (WHO 2017)	KZ limits (Kazakhstan 2015)		W1	W2	W3	W4	W5	W6	W7	W8	W9	Effluents
pH	6.5–8.5	6–9	Range	7.2–8.8	7.5–9.0	8.0–9.1	7.9–9.3	8.5–9.5	8.7–9.5	6.9–9.1	8.3–9.1	6.9–8.7	
			Mean	8.3	8.2	8.6	8.8	8.8	9.0	8.6	8.7	8.1	
			SD	0.4	0.5	0.4	0.4	0.3	0.2	0.6	0.2	0.7	
TPH	0.1	0.1	Range	0.16–1.04	0.11–1.40	0.09–0.60	0.11–0.84	0.08–1.20	0.14–0.67	0.23–0.78	0.11–0.99	0.26–0.84	0.68–2.15
			Mean	0.44	0.41	0.29	0.39	0.40	0.41	0.51	0.45	0.52	1.23
			SD	0.25	0.38	0.14	0.24	0.33	0.17	0.19	0.28	0.18	0.40
TDS	1000	1000	Range	846–1582	4728–7727	1346–2224	643–2919	899–1450	683–1402	1244–1933	1157–1927	28,202–36,392	4–9
			Mean	1156	6307	1779	2072	1218	1046	1485	1470	31,848	7
			SD	185	952	299	561	172	203	205	298	2922	1
Cl^-	250	350	Range	98–211	2450–4410	150–520	56–715	160–4410	110–200	150–370	180–798	10,000–24,757	50–135
			Mean	158	3285	256	425	549	172	256	322	14,797	83
			SD	32	577	90	165	1161	24	62	150	3372	26
SO_4^{2-}	250	500	Range	94–210	544–1300	252–520	127–1100	89–284	150–849	214–296	305–443	4126–9400	238–589
			Mean	164	974	379	670	208	298	260	351	7040	449
			SD	33	190	85	231	46	179	22	39	2086	91
Phenols**	–	0.25/0.001	Range	0.00–0.04	0.00–0.01	0.00–0.06	0.00–0.06	0.00–0.06	0.00–0.06	0.00–0.05	0.00–0.05	0.00–0.12	0.01–0.03
			Mean	0.01	0.00	0.01	0.01	0.01	0.01	0.01	0.01	0.02	0.02
			SD	0.01	0.00	0.01	0.02	0.02	0.02	0.01	0.01	0.04	0.01
NH_4^+	1.5	2	Range	0.0–1.0	0.0–27.1	0.0–0.8	0.0–0.6	0.0–8.6	0.0–5.6	0.0–8.8	0.0–10.9	0.0–25.8	38.6–54.3
			Mean	0.4	2.8	0.3	0.3	0.9	0.7	1.0	1.2	5.6	49.3
			SD	0.3	7.4	0.3	0.2	2.3	1.5	2.4	2.9	7.9	6.0
NO_2^-	3	3	Range	0.0–0.6	0.0–2.0	0.0–1.1	0.0–0.7	0.0–0.4	0.0–0.4	0.0–0.7	0.0–0.9	0.0–14.5	0.1–4.4
			Mean	0.1	0.2	0.2	0.1	0.1	0.1	0.2	0.1	1.5	0.1
			SD	0.2	0.6	0.3	0.2	0.1	0.1	0.2	0.3	4.2	1.3
NO_3^-	50	45	Range	0.0–7.5	0.1–4.3	0.1–3.0	0.0–5.0	0.0–5.3	0.0–4.9	0.0–4.3	0.0–4.1	0.0–21.0	1.8–16.4
			Mean	2.3	1.7	0.9	1.5	1.8	0.9	1.3	1.5	7.7	12.5
			SD	2.9	1.2	0.9	1.6	1.9	1.4	1.6	1.6	8.1	4.0
PO_4^{3-}	–	3.5	Range	0.00–0.75	0.00–0.26	0.00–0.20	0.00–1.00	0.00–0.68	0.00–0.41	0.00–0.21	0.00–0.76	0.00–0.08	
			Mean	0.11	0.04	0.05	0.10	0.10	0.06	0.06	0.10	0.03	
			SD	0.21	0.07	0.06	0.27	0.18	0.11	0.07	0.21	0.02	
CO_3^{2-}	–	–	Range	0–48	0–15	0–87	5–59	6–36	13–84	0–137	0–73	0–45	
			Mean	15	6	30	32	20	31	39	26	11	
			SD	15	5	28	17	8	18	37	19	13	

Table 1 continued

Parameters	WHO limits* (WHO 2017)	KZ limits (Kazakhstan 2015)		W1	W2	W3	W4	W5	W6	W7	W8	W9	Effluents
HCO_3^-	384***	–	Range	189–494	14–391	329–709	43–514	262–512	201–346	9–578	210–329	66–464	
			Mean	375	119	537	326	343	277	374	264	201	
			SD	92	126	100	110	74	42	176	37	138	
TH	–	7.0	Range	3.7–12.5	6.2–67.9	3.2–9.8	3.0–12.0	2.1–5.0	2.0–4.8	2.4–9.3	2.8–15.1	219.0–390.0	
			Mean	7.6	54.0	6.8	7.6	3.9	3.8	6.5	6.5	272.0	
			SD	2.0	15.6	1.7	2.6	0.9	0.9	1.7	3.5	55.0	
Ca^{2+}	100	–	Range	14–116	15–625	6–73	8–138	6–44	5–43	3–137	9–72	97–2844	
			Mean	39	135	21	29	14	13	27	20	497	
			SD	30	154	17	34	10	10	36	16	714	
Mg^{2+}	50	–	Range	17–92	65–680	5–330	31–130	14–88	12–61	25–110	21–200	382–4422	
			Mean	63	499	88	78	42	39	66	66	2697	
			SD	20	196	78	32	18	13	25	44	940	
K^+	12	–	Range	0.1–3.0	0.0–6.4	0.0–5.0	0.0–6.0	0.0–5.0	0.0–4.0	0.0–6.0	0.0–4.0	0.01–42.0	
			Mean	1.5	1.7	1.4	1.6	1.5	1.4	1.8	1.6	14.3	
			SD	1.0	2.1	1.6	2.3	1.7	1.2	2.2	1.4	16.2	
Na^+	200	200	Range	140–230	605–1414	390–685	66–775	220–540	200–500	290–560	220–680	5100–9200	
			Mean	190	1136	480	545	348	296	390	412	7093	
			SD	27	272	85	181	94	77	79	135	1377	
Surfactants	–	0.5	Range	0.1–0.7	0.2–0.6	0.1–0.6	0.0–0.4	0.0–0.4	0.0–0.8	0.3–0.9	0.0–0.4	0.3–1.4	0.2–0.5
			Mean	0.4	0.3	0.4	0.2	0.2	0.2	0.6	0.1	1.0	0.3
			SD	0.2	0.1	0.2	0.1	0.1	0.2	0.2	0.1	0.3	0.1
CO_2	–	–	Range	0–37	0–22	0–29	0–15	0	0	0–23	0–2	0–32	
			Mean	5	5	4	1	0	0	2	0	7	
			SD	11	7	9	4	0	0	6	1	12	

– non-described

*WHO does not cover all chemical contaminants in the guidelines, but only those, which pose a risk in a high level (Gadgil 1998)

**EPA, EU and WHO present a range of phenol-derivatives according their toxicity rate. Kazakhstani standard assumes "phenols" as phenolic compounds, which evaporate under high temperature (Angelino and Gennaro 1997)

***From WHO Guidelines for drinking water quality (1984)

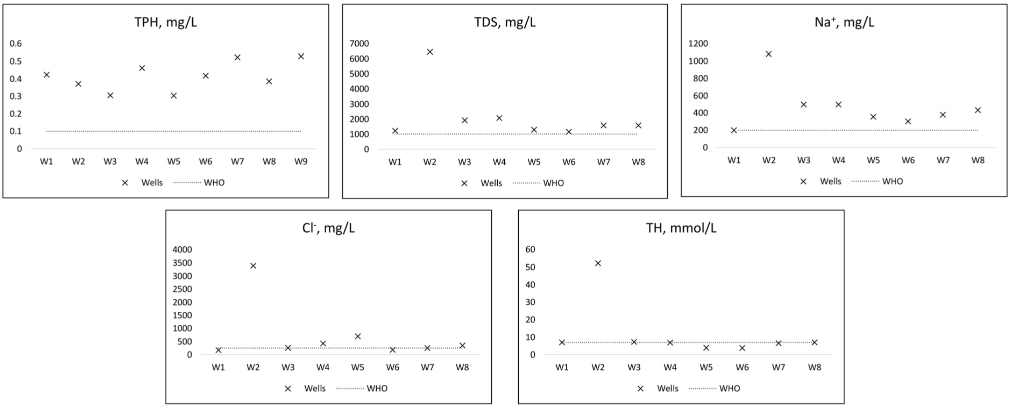

Fig. 5 Concentrations of some chemicals in the groundwater wells compared to WHO limits

permissible KZ limits and WHO indirect recommendation (Fig. 5). Consumption of high amount of sodium has been correlated with cardiovascular disease, such hypertension and stroke (Lucas et al. 2011). Finally, individual exceedings of surfactants were identified. Such high level of surfactants is related to several potential problems. The presence of some surfactants in connection with other contaminants may decrease the biodegradation rate of contaminant or stops the process at all. In other cases, the presence of the surfactants enhances the biodegradation rate. The desirable result is not clear without knowing the role of the surfactant participating the biodegradation process in a given remediation plan (West and Harwell 1992). Moreover, special focus should be paid to Well 9 which had extremely high values. For example, TDS had a value 37 times above the limit, chloride 99 times higher than limit, sulphate exceeded the limit 38 times, total hardness with associated cations by 56 times as well as highly elevated concentrations of ammonia, nitrites, nitrates, potassium, sodium and surfactants (Table 1). This is the reason why Fig. 5 does not include Well 9 presenting the concentrations of some chemicals comparatively with WHO recommendations.

The water containing such levels of those substances would normally be rejected by consumers. Additional epidemiological research should be provided in municipalities nearby the area of pond to assess potential connections between the high concentrations of some parameters, such as TPH, phenols, Na^{+}, Cl^{-}, SO_4^{2-}, TDS and TH and cardiovascular and oncological diseases in the region.

Figure 6 shows temporal distribution of some chemicals. The pH values (Fig. 6a) normally were highest during the spring, while the value for W9 differs significantly and instead shows the lowest values during the same period. It could be explained by influence of recharge of snowmelt and geological characteristics of the area. The same situation can be applied for TPH. All wells show the highest concentrations of TPH during the spring (Fig. 6b). Moreover, the graphs mainly tend to raise their fluctuations and display an increasing trend. It potentially says that the pollution problem is growing in the area. Figure 6c represents the fluctuation of TDS in the groundwater. There are relatively flexible lines without significantly extremal changes.

Spatial distribution of the chemicals is presented in Fig. 7. pH values (Fig. 7a) are more than 7 for all wells, defining groundwater alkaline. According to Hem (1970) dissociation of carbonate and carbonate salts is a dominant process in nature, which leads to pH above 7. The maximal value of pH is found in well 6, and minimal value belongs to the wells 2 and 9. Piper diagram is widely used to show the dominant hydrogeochemical faces (Piper 1944). The Piper plot (Fig. 8) verifies the direct relationships between the hydrochemical regime of groundwater in the area and the pH value. Total petroleum hydrocarbons have a maximal value in the well 9 and minimal in the well 3 (Fig. 7b). There are plotted only TDS, instead of TH,

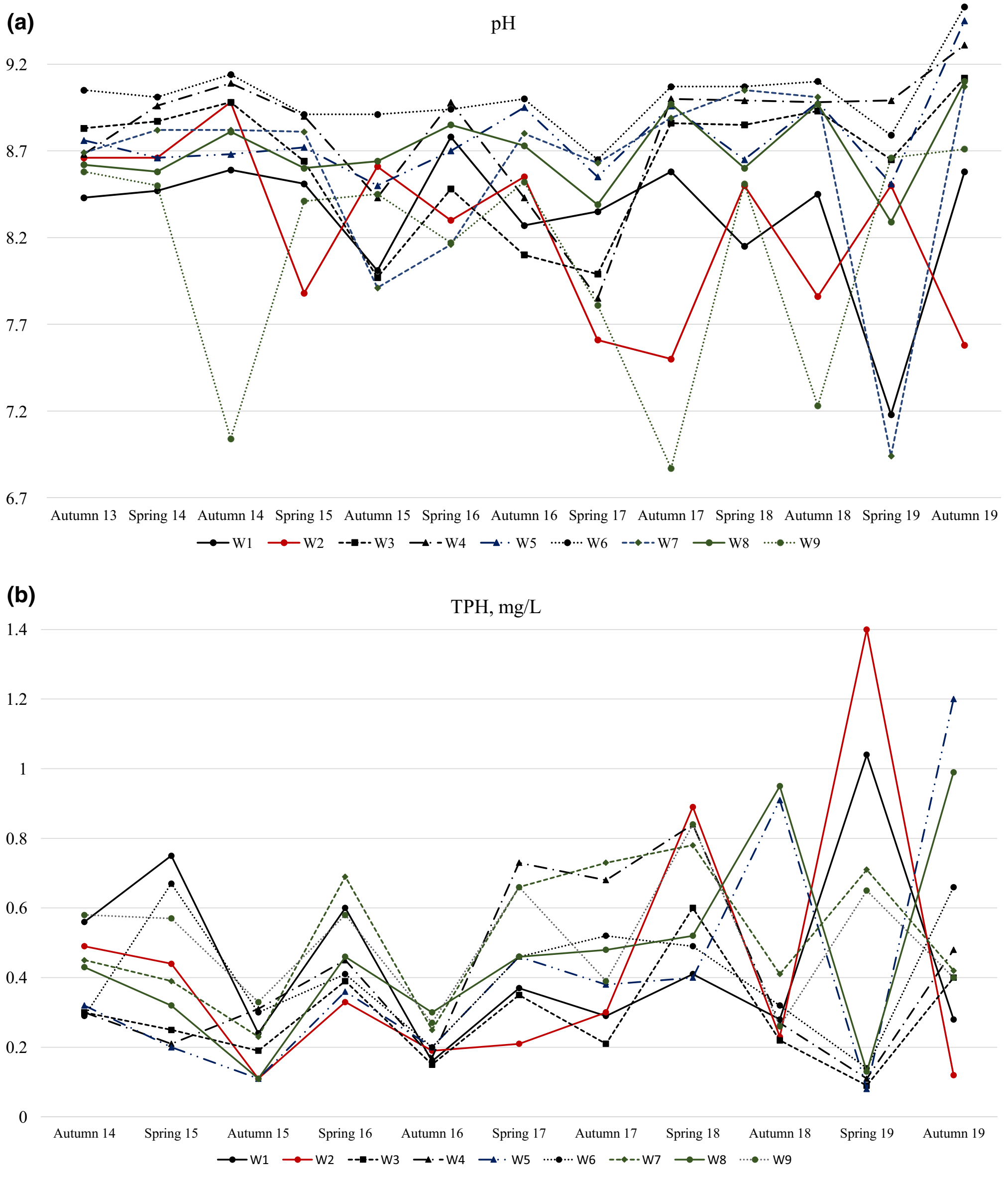

Fig. 6 Temporal variation of **a** pH, **b** TPH and **c** TDS

Ca^{2+}, Mg^{2+}, Na^{+}, Cl^{-} and SO_4^{2-}, on the figure, because they are parts of the TDS and distributed in the same manner (Fig. 7c). Thus, we can consider from the hydrogeological characteristics of this site (Fig. 4) and spatial distribution of pH and pollutants (Fig. 7) that groundwater flow has a slope toward western direction from the pond.

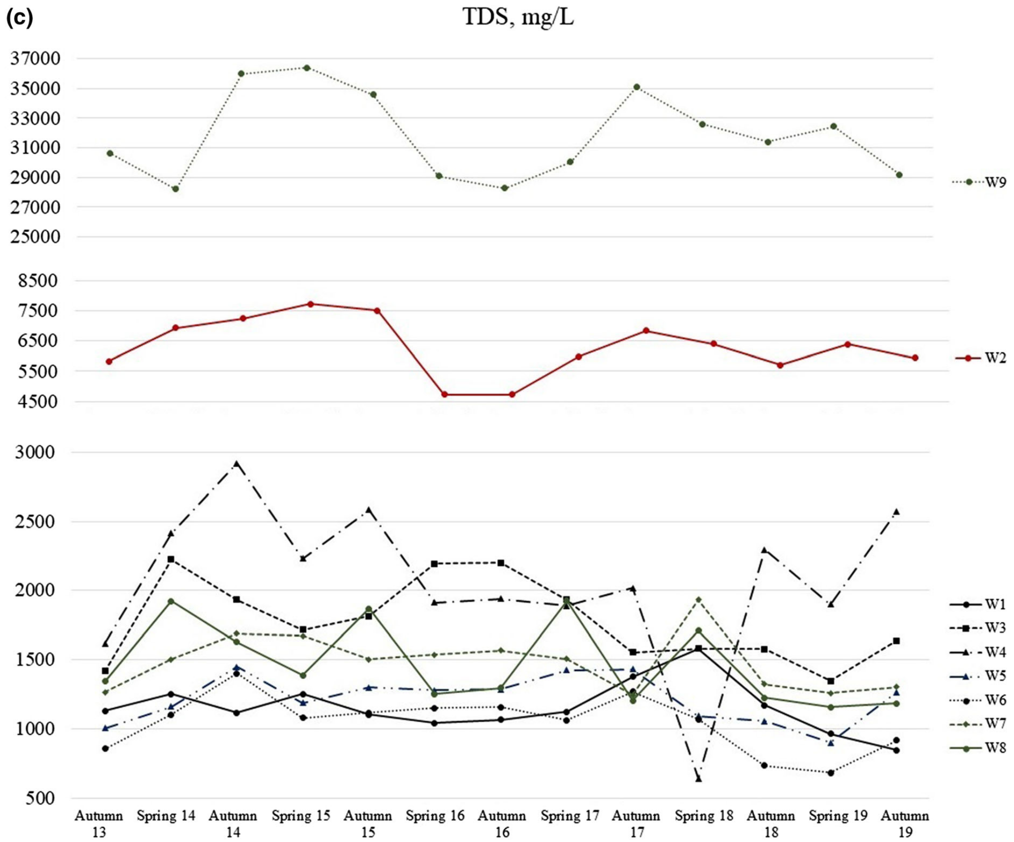

Fig. 6 continued

Principal component analysis

The correlation matrix (Table 3) was employed for all 117 measurements for determining the loads of the principal components (PCs) shown in Table 2. The first six PCs were selected for the following reasons as variables of dimensionality reduction: the six PCs together gave a cumulative contribution of 78.34%, which is typically regarded as being sufficiently high; the eigenvalues of these PCs are all greater than 1.0 and, according to the Kaiser criterion these PCs must be chosen (Table 2) (Kaiser 1958). The factors can be conditionally divided into two groups. First group accounts to 52.34% of the total variance and is represented by Factors 1 and 2. Usually, the parameters, belonging to those factors, characterize natural conditions of the groundwater. Factors 3–6 contribute to 26% of the total variance and can be categorized, as anthropogenically appeared factors. The detailed interpretation of each Factor is explained below.

PC 1

PC 1 explains 42.02% of the total variance (Table 2). It is characterized by high positive weight values TH, Ca^{2+}, Mg^{2+}, TDS, Na^{+}, K^{+}, Cl^{-}, SO_4^{2-} and surfactants. As Table 3 indicates, there is a strong positive correlation between TDS and Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, SO_4^{2-}, Cl^{-}. These ions are the major contributors to the total dissolved solids. Additionally, these ions correlate with each other. These results show that the groundwater has suffered serious mineralization

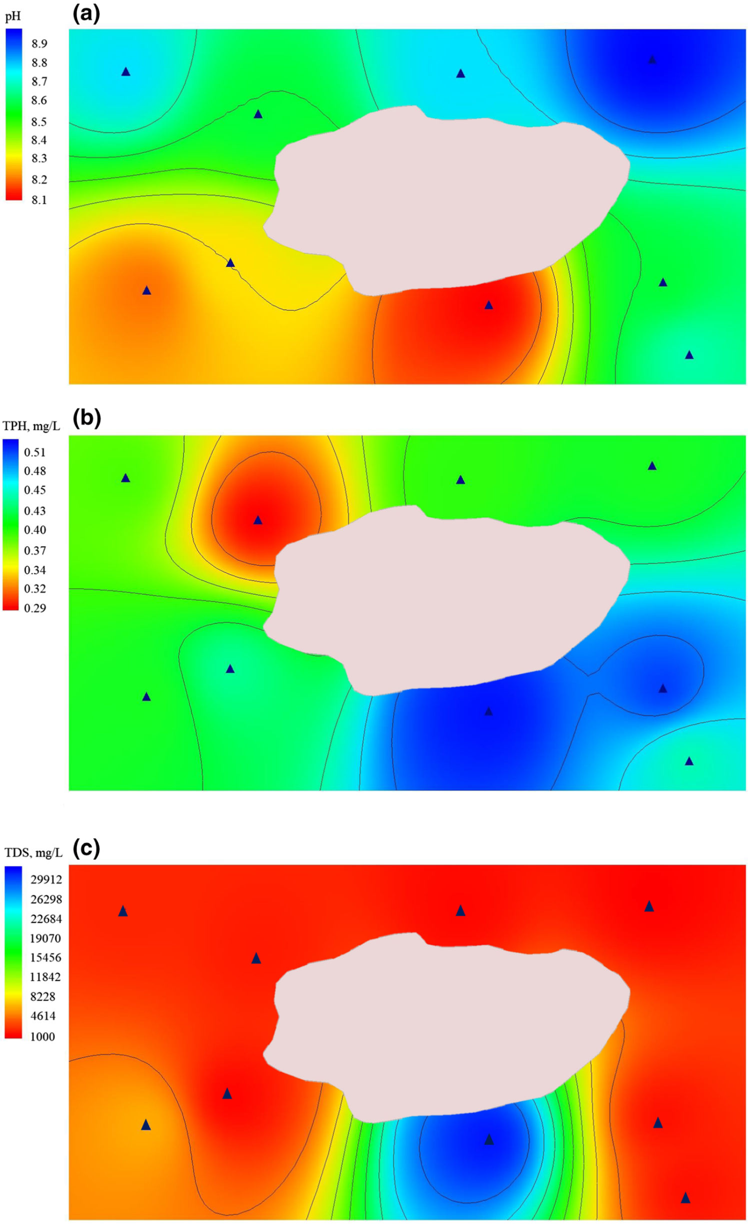

Fig. 7 Spatial distribution patterns of **a** pH, **b** TPH and **c** TDS

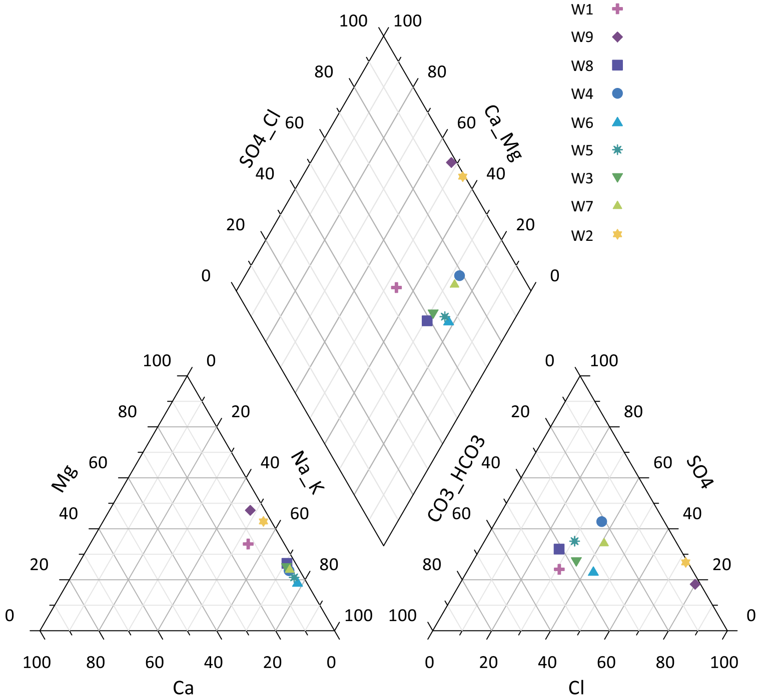

Fig. 8 Piper diagram for identification of water type of the study area

process from the natural condition of the salt pond (Allen and Suchy 2001). Moreover, since TDS correlates with surfactants and surfactants correlate with the above-mentioned ions, it is clear that there is a similarity across parameters.

There also is a clear correlation between TH and subsequent ions: Ca^{2+}, Mg^{2+}, Cl^{-}, ${SO_4}^{2-}$ (Table 3). In addition, it can be seen that all these ions correlate with each other. This correlation points to the existence of non-carbonate, or constant hardness, ($MeSO_4$, $MeCl_2$, where Me—Ca, Mg), which is difficult to remove. It is clear from Table 3 that there is no correlation between carbonate ions and the hardness metals ions, which suggests a weak temporary hardness. This factor can be explained by the natural conditions of the site. In contrast, surfactants are synthetic compounds. Surfactants are produced for cleaning and washing operations (West and Harwell 1992). Their existence in groundwater is not natural.

PC 2

PC 2 explains 10.32% of the total variance (Table 2) with negative weight values of pH and ${CO_3}^{2-}$, and positive value of CO_2. It is important to note a correlation between CO_2, ${CO_3}^{2-}$ and pH (Table 3), which points to alkalinity reactions in the groundwater (Eq. 6). The relationship exists between these parameters and CO_2, which potentially could be described a process of CO_2 creation or the presence of the CO_2 as an atmospheric gas in the unsaturated zone (Hem 1970). Moreover, the high concentration of chlorides in wastewater coupled with the natural salt water leads to changing pH in groundwater by decreasing pH. These processes are naturally based.

$$\mathrm{Alk} = 2\left[\mathrm{CO_3^{2-}}\right] + \left[\mathrm{HCO_3^{-}}\right] + \left[\mathrm{OH^{-}}\right] - \left[\mathrm{H^{+}}\right]. \qquad (6)$$

PC 3

Factor 3 is characterized by a positive value of nitrite ion (Table 2) and contributes 7.68% to the total

Table 2 Factor loadings (Varimax normalized)

Variable	Natural		Anthropogenic			
	Factor (1)	Factor (2)	Factor (3)	Factor (4)	Factor (5)	Factor (6)
pH	− 0.233	**− 0.900**	− 0.045	0.042	0.023	0.014
TPH	0.102	− 0.034	− 0.267	**0.746**	− 0.024	− 0.201
TDS	**0.924**	0.205	0.171	0.158	− 0.002	− 0.058
Cl^-	**0.888**	0.251	0.203	0.146	− 0.086	− 0.058
SO_4^{2-}	**0.927**	0.086	0.203	0.063	0.041	− 0.046
NH_4^+	0.289	− 0.045	0.198	**0.783**	− 0.051	0.162
NO_2^-	0.254	− 0.059	**0.797**	− 0.075	− 0.173	− 0.004
NO_3^-	0.514	0.012	0.500	− 0.031	0.363	0.121
PO_4^{3-}	− 0.100	0.041	0.012	− 0.039	0.027	**0.886**
CO_3^{2-}	− 0.140	**− 0.692**	− 0.074	− 0.010	− 0.023	− 0.337
HCO_3^-	− 0.297	− 0.159	− 0.120	0.026	0.460	0.208
TH	**0.927**	0.160	0.147	0.188	0.053	− 0.033
Ca^{2+}	**0.729**	− 0.069	− 0.382	− 0.182	− 0.231	0.092
Mg^{2+}	**0.798**	0.215	0.326	0.313	0.085	− 0.050
K^+	**0.807**	− 0.032	− 0.375	− 0.106	0.008	0.039
Na^+	**0.931**	0.150	0.196	0.133	− 0.004	− 0.045
Surfactants	**0.732**	0.131	0.107	0.165	0.085	− 0.116
CO_2	0.094	**0.845**	− 0.133	− 0.025	− 0.013	− 0.165
Phenol	0.196	0.078	− 0.015	− 0.077	**0.873**	− 0.086
Eigenvalue	7.984	1.960	1.458	1.307	1.160	1.015
% of variance	42.023	10.315	7.676	6.881	6.105	5.340
Cumulative %	42.023	52.337	60.013	66.894	73.000	78.339

variance. NO_2^- does not correlate with any chemicals. The presence of the parameter could be explained as a semi-product of the natural denitrification/deammonification processes in the groundwater environment according to Hisckock et al. (1991).

PC 4

TPH and ammonia ion represent PC 4 and account for 6.89% of the total contamination (Table 2). Both chemicals have no correlation according Table 3, which shows their independence on the other variables. This level of petroleum hydrocarbons in drinking water can lead to damage of the nervous system and carcinogen and narcotic effects associated caused by some hydrocarbons (Logeshwaran et al. 2018). In addition, even a few micrograms of TPH per litre deteriorate the odour and taste of the contaminated water. The high loading of NH_4^+ is associated with extremally high concentrations of ammonia in discharges (Radelyuk et al. 2019). Hence, the amount of ammonia is not degraded during the saturation processes and some traces still presence in the groundwater. This factor is certainly attributed to groundwater pollution from the petrochemical industry.

PC 5

PC 5 is characterized by positive value of phenols (Table 2), which accounts for 6.11% of the whole contamination. This parameter is characterized as a very toxic pollutant. Concentrations of the phenolic compounds probably exceed the permissible level (Table 1); the exposure is evaluated as a potential risk for public health. The loading of this parameter is directly related to the specification of petrochemical wastewater.

Table 3 Pearson correlation matrix for 19 hydrochemical variables (whole dataset)*

	pH	TPH	TDS	Cl^-	SO_4^{2-}	NH_4^+	NO_2^-	NO_3^-	PO_4^{3-}	CO_3^{2-}	HCO_3^-	TH	Ca^{2+}	Mg^{2+}	K^+	Na^+	Surfactants	CO_2	Phenol index
pH	**1**	0.062	− 0.389	− 0.420	− 0.296		− 0.061	− 0.148		**0.578**	0.164	− 0.342	− 0.132	− 0.346	− 0.141	− 0.354	− 0.373	**− 0.731**	− 0.072
TPH		**1**	0.132	0.106	0.117	0.344	− 0.070		− 0.128		− 0.165	0.142		0.140	0.175	0.123	0.188		
TDS			**1**	**0.971**	**0.941**	0.373	0.290	0.479	− 0.117	− 0.235	− 0.307	**0.972**	**0.509**	**0.942**	**0.607**	**0.979**	**0.715**	0.234	0.171
Cl^-				**1**	**0.878**	0.380	0.324	0.475	− 0.119	− 0.251	− 0.339	**0.934**	**0.513**	**0.915**	**0.567**	**0.951**	**0.683**	0.287	0.096
SO_4^{2-}					**1**	0.307	0.404	**0.516**	− 0.106	− 0.198	− 0.282	**0.914**	**0.520**	**0.847**	**0.667**	**0.926**	**0.734**	0.130	0.222
NH_4^+						**1**	0.166	0.238		− 0.089		0.419	0.131	0.499	0.101	0.373	0.300	− 0.059	− 0.062
NO_2^-							**1**	0.464		− 0.069	− 0.157	0.256		0.304		0.335	0.276		− 0.070
NO_3^-								**1**		− 0.215	− 0.124	**0.504**	0.181	**0.504**	0.342	**0.512**	0.432		0.347
PO_4^{3-}									**1**	− 0.125	0.070	− 0.115	− 0.085	− 0.100	− 0.081	− 0.113	− 0.129		
CO_3^{2-}										**1**	0.124	− 0.238	− 0.098	− 0.237	− 0.138	− 0.208	− 0.075	− 0.353	− 0.091
HCO_3^-											**1**	− 0.307	− 0.186	− 0.271	− 0.193	− 0.310	− 0.100	− 0.112	0.063
TH												**1**	**0.521**	**0.945**	**0.628**	**0.961**	**0.706**	0.178	0.228
Ca^{2+}													**1**	0.299	**0.713**	**0.558**	0.391	0.080	
Mg^{2+}														**1**	0.409	**0.925**	**0.641**	0.199	0.213
K^+															**1**	**0.592**	**0.532**	0.127	0.148
Na^+																**1**	**0.705**	0.181	0.183
Surfactants																	**1**	0.184	0.126
CO_2																		**1**	0.068
Phenol index																			**1**

*Insignificant coefficients at the 0.05 level are removed. Bold values represent significant coefficients higher than 0.5

PC 6

One more significant factor belongs to the influence of phosphate-ions and is rated by 5.34% of the total variance (Table 2). It should be pointed out that the enterprise does not provide monitoring of phosphate concentration in the discharges. Nevertheless, the refining process is associated with a vast number of washing processes, which leads to big consumption of different detergents, which contain phosphate substances. As the rocks and fertilizers are absent in the study area (Rao and Prasad 1997), we can conclude that the loading of the contaminant is an indicator of anthropogenic impact on the groundwater.

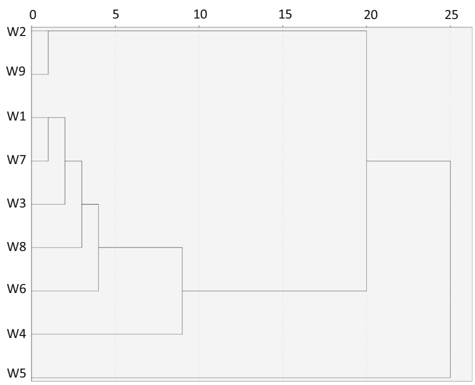

Fig. 9 Dendrogram showing clustering of sampling sites according to groundwater characteristics (Ward Linkage. Euclidean Distance)

Table 4 Selected variables characteristics*

Variable	Toxic	Non-toxic
Number of observations	324	351
	48.0%	52.0%
Number (%) of exceeded values	255 (78.7)	248 (70.7)
Dependent variables		
Toxic contaminant	1.0	0.0
% of exceeding	664 (1042)	862 (1526)

*Statistics of chosen chemicals is available from Table 1

Cluster analysis

Based on the performed CA and results above, the study area was divided into three clusters. Figure 9 shows a dendrogram of all nine sampling sites into three statistically meaningful clusters yielded by cluster analysis. Cluster 1 combines observed wells W9 and W2. These wells are labelled as highly contaminated with the highest exceeding of many chemical parameters. Figure 4a shows their similarities in the distribution of pH, which is followed by host geology. The wells are situated on the southwest site from the pond and probably approve an assumption about direction of groundwater flow. Cluster 2 is formed by wells W7, W8, W1 and W3. These wells are located on the south and west sides of the pond and characterized by twofold characteristics: firstly, significant pollution rate, including the same concentrations of the TDS and TDS related chemicals and secondly, the equal temporal distribution of pH. It means that groundwater on that site is affected by pollutant transport from the pond in the same manner. Finally, Cluster 3 is represented by wells W6, W4 and W5. All wells are located north of the pond and are characterized by lower concentrations of the pollutants compared to other wells. We may consider that groundwater flow originates from east to west, and potential hazard exists for rural inhabitants towards to west and south-west direction from the pond.

The Heckman selection model

This study uses the Heckman selection model to estimate relationships between total contamination and other characteristics, especially, significance of toxicity rate. If we adapt Eqs. (4) and (5) for our case

Table 5 Estimated results of the Heckman selection model (two-step) for selected chemicals

Variable	Coefficient	Std. Err	Z-statistic
Chemical	− 0.156	0.074	− 2.11
Concentration	1.576	0.260	6.07
Toxicity rate	0.789	0.245	3.22
Number of well	0.020	0.025	0.83
Rho	1.0		

according Stata manual (STATA 2013), we can represent the equations respectively as:

$$\% \text{ of exceeding } = \beta_1 \text{chemical } + \beta_2 \text{concentration} + u_i, \tag{7}$$

and we assumed that "% of exceeding" is estimated if

$$\gamma_1 \text{toxicity } + \gamma_2 \text{number of well} + \gamma_3 \text{chemical} \gamma_4 + \text{concentration } + v_i > 0, \tag{8}$$

where *ui* and *vi* have positive correlation ρ.

Table 4 shows the selected variables used in this analysis and their descriptive statistics. The first dependent variable (D_i) represents toxicity of the chosen chemical. The value equals 1 if the pollutant is toxic and 0 if not. The second set of dependent variables (Y_i) includes percentage of exceeding. This characteristic mathematically represents rate of contamination. Mean percentage of selected (toxic or non-toxic) exceeding was calculated. For example, if the concentration of TPH measurement was 0.25 mg/L, but standard value is no more than 0.1 mg/L, then dependent variable equals 250%. This variable includes only exceeded values. Otherwise, if the value is normal, a cell in a matrix is empty. Numbers in parentheses are standard deviations of the average values. Set of control variables (X_i) includes chosen contaminants, their concentrations and locations. According requirements (Kazakhstan 2015), TH, TPH, and Na^+ are considered as hazardous for public health and rated with value 1.0 for the variable D_i. TDS, sulphates and chlorides are considered as non-toxic and were rated as value 0.0 for the variable D_i. We encrypted TDS, Cl^-, SO_4^{2-}, Na^+, TH and TPH in the table of variables as "1", "2", "3", "4", "5" and "6", respectively. The contaminants are not a subject for assessment in this analysis.

Table 5 presents the estimation for this type of analysis. Rho has a positive value, which means that it is possible to estimate relationships between chosen variables and final contamination. All variables, excluding number of well (which represents location of the wells), are considered as significant. The concentration of pollutants has the greatest influence on total contamination. Positive value explains likelihood of potential hazard for people health. Obviously, the high concentrations of the pollutants lead to deterioration of health, especially during long-term exposure. In our case, 503 of 675 values exceed acceptable limits by 7–8 times averagely. The variable of toxicity rate is the second significant factor. This variable reflects to lower percentage of exceedings for toxic contaminants than for non-toxic, instead of higher number of exceeded values for toxic contaminants than non-toxic. Our hypothesize assumes that even if the concentration of the toxic contaminant exceeds the standard by just a few units, the toxic properties could be much more dangerous for human health, compared with the consumption of highly polluted water by non-toxic contaminants. The independent chemicals represent the third significant variable. Individual characteristics of chosen chemicals are explained in sub-section "Groundwater quality parameters". The location of the well is rated as not significant parameter. Nevertheless, the investigation of hydrogeological characteristics deserves attention in the future work and determines the spread of contamination.

Conclusions

This study investigated the current situation of groundwater safety for public health surrounding a contaminated site in Kazakhstan. The results show that PCAs have high loading of anthropogenic contamination to groundwater from the oil refinery industry coupled with natural geochemical processes. In addition, exceeding concentrations of hazardous substances, including TPH, phenols, TH, and TDS were identified. By means of cluster analysis we were able to combine the examined wells in three groups according to the concentrations of chemicals and their locations. Highly polluted groundwater was distributed especially in west and south-west direction from the pond. The results enable the prediction of the groundwater flow in the study area as well as the estimation of sites heavily affected by contamination. The usage of Heckman selection model, to the authors' knowledge, is the first attempt in the literature, applied to evaluation of environmental factors. According to obtained data from Heckman analysis, focus should be paid to the distribution of toxic contaminants.

For this purpose, further research considers: (1) Groundwater modelling for definite identification of groundwater flow and potentially affected rural areas;

(2) Contamination transport modelling, as the industry continue polluting the environment, the assessment of present and future hazards is highly needed; (3) Development of a remediation plan, which has to be built on the qualitative studies (1) and (2).

This study might be used as a trigger to drive and engage all stakeholders into the transparent dialogue about potential consequences of non-sustainable wastewater management at oil refinery industry. The potential actions might include implementation of successful legislative standards, development of new efficient monitoring programs, stimulation the industry to innovative and water-saving treatment methods and a creation of a site contamination/remediation programs.

This research has several limitations. Firstly, the limited dataset covers only period from 2013 to 2019. Secondly, despite of the concentrations of TPH are identified, the lack of data on specific hydrocarbon type such as PAH and BTEX limited the analysis on the toxicity. Thirdly, the lack of access to hydrogeological data limited the accuracy of the ground water flow estimation. Authors of this paper recommend initiating a dialogue between industry, government, and academia for research-based decision-making in this area.

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Compliance with ethical standards

Conflicts of interest The authors declare no conflict of interest.

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Paper III

Assessing data-scarce contaminated groundwater sites surrounding petrochemical industries

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Abstract: A common problem when studying groundwater contamination in low-income countries is that data required for a detailed risk assessment are limited. This study presents a method for assessment of the potential impact of groundwater contamination by total petroleum hydrocarbons (TPH) in a data-scarce region. Groundwater modeling, using the MODFLOW, was used to simulate regional scale flow pattern. Then, a semi-analytical contamination transport model was calibrated by minimization of the absolute errors between measured and modeled concentrations. The method was applied to a case study in Kazakhstan to assess the potential spreading of a TPH plume, based on historical observations. The limited data included general information about the local geology, observations of GW level in the area, and concentrations during five years of TPH in monitoring wells surrounding the source of the pollution. The results show that the plume could spread up to 2-6 km from the source, depending on estimate of the initial concentrations, until the concentration reaches permissible levels. Sensitivity analysis identified parameters of longitudinal and transverse dynamic dispersivity together with the plume of TPH spreading, as the priority subjects for future investigations. The proposed approach can be used as a tool for governmental and municipal decision makers to better plan the usage of affected groundwater sites in data-scarce regions. It can also help to decrease the negative impact of contaminated GW on human health and to better manage the industrial pollution.

Keywords: Groundwater contamination, Petrochemical industry, MODFLOW, Contamination transport, Sensitivity analysis, Kazakhstan

1. Introduction

Industrial activities are recognized as major source of pollution worldwide (Hossain 2011). Kazakhstan is a country that currently invests heavily in industrial capacity to develop the economy (UN 2019). Industrial development and economic growth, however, put pressure on environment and may jeopardize environmental safety and wellbeing of society (Li 2016). Several studies have shown that air (Assanov et al. 2021), water (Hrkal et al. 2006; Karatayev et al. 2017), and soil (Mikolasch et al. 2019; Woszczyk et al. 2018) are under pressure from industrial pollution in Kazakhstan. The current severe ecological status in many industrial regions serves as a challenge for the country to enforce environmental assessment, policy, and remediation practices (Russell et al. 2018). Up to 65% of all freshwater resources in Kazakhstan may be permanently lost due to wasteful use and polluting activities. Simultaneously, the industry consumes about 25% of all available freshwater in Kazakhstan (Karatayev et al. 2017). It is projected that the mismanagement of freshwater resources could lead to a national water deficit by 2030 (Thomas 2015).

Processes of water usage in the oil refinery industry in Kazakhstan with consequent environmental pollution have already been described by Radelyuk et al. (2019). While Kazakhstan has declared it will carry out the implementation of Best Available Techniques (BAT) and approaches towards developing a green economy, the mechanisms for implementation of such measures still have loopholes. According to Kazakhstani law, if water in a wastewater discharge point is already polluted and water quality can not be assured as safe for any type of usage, further wastewater discharge may continue without strict limitation (Ministry of Environment 2012). The requirement for this is that the receiving water body should not be used as a source for drinking, domestic use, or irrigation purposes. Also, the impact on groundwater should be eliminated, as even a relatively small pollution discharge may affect the whole aquifer (Naseri-Rad et al. 2020; Water Code 2003). According to Locatelli et al. (2019), when groundwater has been exposed to pollution for decades, the concentration in the aquifer may have achieved quasi-steady-state conditions. In Kazakhstan, many receiving water bodies, such as lakes and ponds, have already been polluted during the Soviet period and the pollution process has been continuing ever since. Thus, industries in Kazakhstan use their legal right to discharge improperly treated wastewater into the environment.

Monitoring of groundwater quality in Kazakhstan is usually carried out by installation of observation wells surrounding the source of contamination. The concentration of contaminants should not exceed the defined limit at a regulated boundary of a sanitary zone, which is defined as being 1000 m downgradient from a contamination source (Ministry of Economy 2015). However, recent research in the experimental area of this study has shown that pollutant concentrations often exceed permissible levels outside the sanitary zone. Consequently, pollutants at some sites are likely to be spreading towards areas with substantial groundwater use (Radelyuk et al. 2021).

According to EU (EU 2002), the following investigations should be considered to analyze existing pressures and impacts of the pollution on environment and health of settlements: (1) groundwater modeling for identification of groundwater flow and potentially affected areas, and (2) contamination transport modeling, as the old industrial spills continue polluting the aquifer. These studies are a basis for further management of the affected area. Groundwater research, a key component of the procedure, is associated with long-term investigations, uncertainty, challenges for cooperation and data sharing between a wide range of stakeholders, and the use of advanced technological measures to determine the likely fate of contaminants in the subsurface (Li 2016). Karatayev et al. (2017) noted, that poor collaboration between key stakeholders (government, industry, and academia) in Kazakhstan is a major weakness for supplying decision makers with quantitative facts. Consequently, the required research faces several limitations.

Under the conditions of lacking relevant data, a holistic view is needed to evaluate the situation and to give input to decision making and actions towards improvement of the ecological status of the affected region. This research is an attempt to deal with the complexity assessing and managing groundwater pollution in a low-income country like Kazakhstan, and to obtain an insight concerning pollution spread in an efficient manner in situations where limited data are available.

The method proposed in this study uses a two-step procedure. The first step includes carrying out numerical groundwater modeling using MODFLOW to define the groundwater flow direction. In the second step, a contamination transport model is applied for general description of plume development in the aquifer. As a result, the potential fate of contaminants can be assessed under consideration of different scenarios, depending on local conditions. The suggested method is applied to a case study where groundwater contamination occurs from a petrochemical industrial cluster in Kazakhstan. The aim is, firstly: to identify the area of the aquifer that would be affected by contamination based on historical observations; and secondly, to assess the potential hazard from the spreading of the contamination in groundwater under different scenarios.

This paper consists of the following sections. The Methodology section includes three parts. Part 1 presents the general procedure of the developed method. Part 2 gives general insights about requirements for each step of the procedure. Part 3 shows, how the method was applied to a real-world case study with limited data. The Results and Discussion present results of the applied method. The

Conclusions section discusses limitations, advantages, and disadvantages of the method, and how the method can be used for real-world problems.

2. Methodology

2.1. Procedure

The procedure developed in the present study is introduced in Figure 1. Firstly, all available data should be collected and screened. Potential data sources are official reports from the government and industry, personal communication, and previous research in nearby areas (Step 1). Secondly, groundwater modeling is performed, using a basic set of information regarding local lithology, boundary conditions, and observed piezometric heads (Step 2). A regional-scale model is developed if the area of investigations is large. After calibration of the regional scale model, local scale modelling is carried out to define the direction of groundwater flow, as a starting point for contamination transport modeling. Modeling result is considered reliable if the estimated hydrogeological characteristics match the values from technical reports and available literature. Finally, contamination transport modeling is carried out to consider real and potential scenarios of contamination within the aquifer (Step 3). A steady state contamination transport model is based on the solution of partial differential equations for advection-dispersion processes. The modeling is considered successful, if the calibrated input parameters to the contamination transport modeling fit the values from the groundwater modelling and available data, including measured against modeled concentrations (McMahon et al. 2001). Then, the obtained parameters are used for estimation of spreading of the contamination plume in space, based on historical records and potential scenarios.

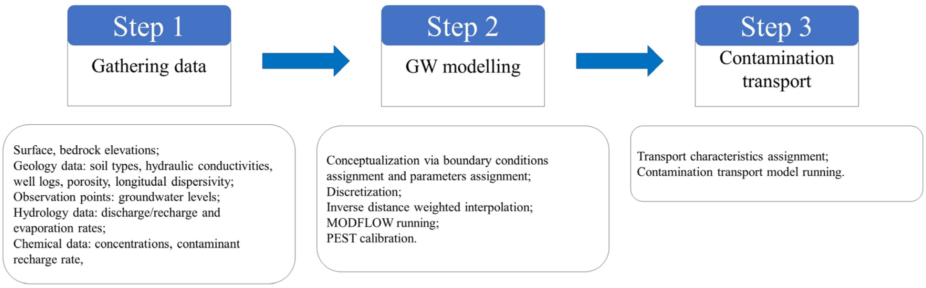


Figure 1. *Schematic of the methodology used in this study.*

2.2. General description of the developed method

2.2.1. Step 1. Data preparation

Data needed for groundwater modeling are obtained from hydrogeological field studies. Modeling of groundwater flow is reliable when geological characteristics such as the properties of the aquifer matrix, the aquifer thickness and bedrock elevations and hydrological properties such as groundwater levels, boundary characteristics, the hydraulic conductivity (HK) of the aquifer matrix, conductance, and other data if they are available (Hashemi et al. 2013; Hashemi et al. 2015). However, data from especially older studies need to be quality controlled. The collected data are used to characterize the aquifer, define boundary conditions, achieve an efficient discretization scheme, and subsequently, to build the groundwater flow model.

Contamination transport modeling requires information about advection-dispersion processes in the porous media, which depends on both properties of geological layers and the contaminant. They include: concentrations of contaminants at the monitoring points to validate the process of contaminant spread and related characteristics; starting concentrations of the pollutants, depending on the source of pollution, and recharge concentrations of the pollutants depending on the load from the source. The required local geological characteristics for transport modelling include longitudinal dispersivity and porosity. Field studies are important and if lacking, uncertainty increases (Naseri-Rad and Berndtsson 2019).

2.2.2. Step 2. GW modeling

After all available data are gathered, a conceptual site model (CSM), which is an efficient tool for presentation and understanding of groundwater flow and transport processes (Todd and Mays 2005), is created. The CSM is a consideration of all hydrogeological processes that control the transport, migration, and any potential and real impacts of contamination in groundwater. The conceptualization includes firstly, assignment of boundary conditions, such as identification and consideration of inflows/outflows/barriers to the system, geometry, receptor(s), interactions between surface water and groundwater, etc.; and secondly, assignment of values for aquifer characteristics (McMahon et al. 2001).

The choice of a modelling approach depends on two factors: the data availability and reflection to the modeling objectives (McMahon et al. 2001). In case of model construction for investigation of groundwater pollution, one of the most popular and efficient tools for GW modeling is MODFLOW-2000, which was developed by McDonald and Harbaugh (Harbaugh et al. 2000). The CSM is represented in a quantitative framework, which is based on the principal equation of the three-dimensional groundwater flow equation for porous medium using a finite-difference method. The Groundwater Modeling System (GMS 9.0) software can be used to perform the modelling under a steady-state condition (Eqn (1)).

$$\frac{\partial}{\partial x}\left(K_{xx}\frac{\partial h}{\partial x}\right)+\frac{\partial}{\partial y}\left(K_{yy}\frac{\partial h}{\partial y}\right)+\frac{\partial}{\partial z}\left(K_{zz}\frac{\partial h}{\partial z}\right)\pm W=0 \qquad (1)$$

where K_{xx}, K_{yy}, and K_{zz} are hydraulic conductivity along the x, y, and z axis assumed to be parallel to the major axes of hydraulic conductivity (m/d); h is the potentiometric head (m); and W is volumetric flux per unit volume, representing sources and/or sinks of water. Steady state modeling is the optimal option for consideration of boundary conditions as well as simulating the general groundwater flow (Hashemi et al., 2012). Thus, steady-state conditions are assumed as the best option under data scarcity, such as lack of information about temporal changes of groundwater level, storage parameters, recharge, and discharge rates.

The next step is the calibration process, which aims to estimate and utilise all available model parameters. Manual (trial and error), automated (e.g., PEST package (Doherty et al. 1994)), and combined (manual and automated) calibration methods can be used to calibrate the model by minimizing the difference between simulated and observed groundwater levels, as those measurements are usually available and are commonly used in the calibration processes (Barnett et al., 2012). The problem with only head data being available is that this parameter on its own cannot mathematically constrain an inverse solution of the groundwater flow equation (Haitjema 2006). This problem can be solved by using other parameters for calibration, such as hydraulic conductivity, conductance, transmissivity and drain values with ranges based on reported available data. The process of calibration is considered successful when the root mean square error (RMSE) residual of head is less than a certain value relevant for local conditions (typically 1 m, as default) (Fienen et al. 2013).

If the aquifer is large with limited data and with an uneven distribution of monitoring wells, it is recommended that a number of groundwater flow models are developed at a regional to a local scale. In this case, all the available information together with the simulated regional groundwater flow direction are transferred to the local model as an initial condition. This will help establish reliable conditions for the model boundaries as well as assigning realistic hydraulic parameter values.

However, the local scale modeling calibration may encounter some problems, as the grid size changes from regional to local scale. This may contribute to increased uncertainty of defining correct pathways of contamination transport. To overcome this, while keeping the same layer data such as bottom, surface, and groundwater elevations, the boundary conditions for the local model are assigned to the specified heads (Mehl and Hill 2010). The model grid is re-discretized if needed within the decreased grids. When the groundwater model is calibrated, a particle-tracking tool for MODFLOW, named MODPATH, can be used to assign the required coordinates for contamination transport modeling via displaying the groundwater flow direction in the study area (Pollock 2012). In this way possible pathways for pollution transport can be determined.

2.2.3. Step 3. Contamination transport modeling

The transport model incorporates steady-state solution for groundwater flow as a starting point to compute how concentrations of dissolved contaminants from a plan source change over time as they are transported in groundwater by advection and dispersion. This accounts for the role of varying hydraulic conductivity and other spatially variable hydraulic parameters that accompany aquifer heterogeneity. The transport model used for this purpose is based on partial differential equations for dispersion that have been developed for homogeneous and isotropic media, where Darcy's law is valid (Ogata and Banks 1961; Ogata 1970; Bear 2013).

Generally, contaminant source concentration and mass discharge in time are not well known at most contaminated sites (Locatelli et al. 2019). According to Sauty (1980), if a tracer is continuously injected into a uniform flow field from a point source, contamination will spread as shown in Figure 2. In this case, flow is governed by Eqn. (2), where mass transport is calculated in two dimensions:

$$\frac{\partial C}{\partial t} = D_L \frac{\partial^2 C}{\partial x^2} + D_T \frac{\partial^2 C}{\partial y^2} - v_x \frac{\partial C}{\partial x} \tag{2}$$

where v_x is down gradient fluid velocity, D_L is longitudinal dispersion coefficient (m^2/d), D_T is transverse dispersion coefficient (m^2/d), and C is solute concentration at x, and y (mg/m^3).

An observation point with known concentration is assumed at location $x = 0$, and $y = 0$ with a uniform flow velocity at a rate v_x parallel to the x axis. Then, a solute is represented with a concentration C_0 at a rate Q over the aquifer thickness, b. The equation to calculate the concentration on a distance from the observation point can be found from a Green function (Bear 2013; Fried 1975) for the injection of a unit amount of a contaminant, under a steady-state condition, is expressed as:

$$C(x,y) = \frac{C_0\left(\frac{Q}{b}\right)}{4\pi(D_L D_T)^{0.5}} \exp\left(\frac{v_x x}{2D_L}\right) K_0\left(\frac{{v_x}^2}{4D_L}\left(\frac{x^2}{D_L} + \frac{y^2}{4D_T}\right)\right)^{0.5} \tag{3}$$

where K_0 is the modified Bessel function of the second kind and zero-order, $C_0\left(\frac{Q}{b}\right)$ is the rate that the contaminant is injected, and b is the thickness of the aquifer over which the contaminant is injected.

Some parameters (i.e., v_x, D_L, D_T, and Q) need to be addressed, prior to solving Eqn. (3). According to Darcy's law, average linear velocity, v_x, is the rate at which the flux of water across the unit cross-sectional area of pore space occurs (Fetter et al. 2018):

$$v_x = \frac{K}{p}\frac{dh}{dl} \tag{4}$$

where v_x is average linear velocity (m/d), K is hydraulic conductivity (m/d), and p = effective porosity, $\frac{dh}{dl}$ = hydraulic gradient (m/m).

Multiplying v_x by the cross-sectional area of the plume makes up the injection rate of the contaminant (Q) to the aquifer:

$$Q = v_x \cdot T \cdot b \tag{5}$$

where T is plume width and b is the thickness of the aquifer over which the contaminant is injected. The longitudinal and transverse hydrodynamic dispersion, D_L and D_T, respectively, can be calculated as:

$$D_L = \alpha_L v_x + D^* \tag{6}$$

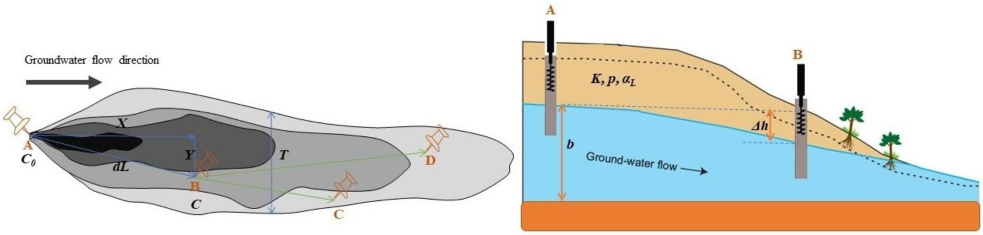
$$D_T = \alpha_T v_x + D^* \tag{7}$$

where $\alpha_L$is longitudinal dynamic dispersivity and α_T is transverse dynamic dispersivity. A value of longitudinal dispersivity may exceed 50 m for long flow fields (Gelhar 1986). The ratio between α_L and α_T can be equal from 6 to 20.

The D^* is an effective diffusion coefficient, which can be calculated as follows:

$$D^* = \omega D_d \tag{8}$$

where ω is a coefficient related to the tortuosity (Bear 2013) and D_d is the diffusion coefficient (m^2/d). However, as D_d is small and ω is always less than 1, the effective diffusion coefficient, D^* is neglected.



X, Y – coordinates
C_0 – initial concentration
C – solute concentration at X, Y
T – plume width

K – hydraulic conductivity
p – effective porosity
dh/dL – hydraulic gradient
α_L – longitudinal dynamic dispersivity

Figure 2. *Conceptual framework of the contamination transport model.*

The solution of the contaminant transport problem (Eqn. (3)) in 2D may be calculated by the Plume2DSS() add-in (Renshaw 2013) in Excel. However, this add-in requires exact values of transport parameters, which are unavailable at the site. Thus, the authors developed an optimizer using Macro in Visual Basic for Application (VBA) in Excel. This Macro solves the Plume2DSS() using an optimizer with multiple iterations within the given range of transport parameters to minimize the absolute error (difference between measured and calculated concentrations at each specific point) for each measurement event.

The model is assigned by the following characteristics: the exact locations of sampling points (x, y, and dL), obtained from the groundwater model; contaminant concentrations; hydraulic gradients between any two wells; and ranges of value changes for transport parameters, i.e., T, b, K, dh, p, α_L, and α_T. The developed code then calculates the concentration at any point downstream by optimizing the calibration parameters in the given range to minimize the error. Once optimal parameters are determined, the model is validated by using these in the Plume2DSS() add-in, and subsequent comparison between $C_{calculated}$ (a concentration, obtained without running the code) and $C_{measured}$. Thus, optimal transport parameters are numerically obtained via minimization of the absolute error.

As a final step, a fate and transport modelling assessment is carried out. Once all required solute transport parameters are defined, new coordinates ($x+x_i$, $y+y_i$, and dL_i) are assigned via extension of the already defined pathways (an example is shown in Figure 2 for the pathways BD and/or BC) and C_i ($x+x_i$, $y+y_i$) is solved using Eqn. (3).

The proposed method was applied to the case study to illustrate its applicability in a real-world (although admittedly a complex) environmental problem. The complexity in this case study comes from the heterogeneous geology at the site and the persistent and uncertain nature of the contamination.

2.3. Study area description

The Pavlodar region is one of the largest industrial centres in Kazakhstan. Metallurgical, chemical, and petrochemical industrial activities have been causing the environmental condition of the region. The local petrochemical industry is a major actor in the economic activities and the main taxpayer in the region, which accounts for about 50% of the city budget (Neftepererabotchik 2019). As residents of the rural area near the industrial zone are using the groundwater from the shallow aquifer for their drinking and domestic purposes (Tussupova et al. 2016), an investigation was needed to assess potentially affected sites and to prevent members of the local community from drinking unsafe water. The source of potential contamination in this case study is a recipient pond "Sarymsaq" (Appendix A), where wastewater is discharged by the cluster of local petrochemical industry sites (Radelyuk et al. 2021).

The wastewater from the oil refineries is mainly characterized by petroleum hydrocarbons (Alva-Argaez et al. 2007). Even after primary mechanical treatment, it is difficult to remove hydrocarbons from the wastewater (Bruno et al. 2020). The most basic biological treatment method, activated sludge, which is used by refineries in Kazakhstan, cannot efficiently treat the wastewater for two reasons: firstly, because the petroleum hydrocarbons have a low level of biodegradability; and, secondly, because the salinity and toxicity of wastewater inhibits the efficiency of the treating biomass.

While developed countries have identified certain indicators, such as polycyclic aromatic hydrocarbons (PAHs), or benzene, toluene, ethylbenzene, xylenes (BTEX), for the better estimation of toxic effects from wastewater (CONCAWE 2018; USEPA 2019), Kazakhstani oil refineries monitor only the sum of total petroleum hydrocarbons (TPH), without an assessment of the constituent potentially toxic chemical compounds. The term TPH describes the range of hundreds to thousands of individual compounds. Previous research has shown that hydrocarbons, originating from the petrochemical industry, are practically ubiquitous in groundwater, are usually only biodegraded to a limited extent, and the resulting contaminant plumes may be several kilometers long (Balderacchi et al. 2013). Measured concentrations in groundwater samples show that the amount of TPH constantly exceeds the permissible limit in all monitoring wells surrounding Sarymsaq, which confirms the presence of groundwater pollution in the area (Radelyuk et al. 2021). The amount of TPH usually has maximum peaks during the spring season, which can be explained by intensive snowmelt and large infiltration of water through the soil profile.

2.3.1. Step 1. Data preparation

The following sources of information were used for this study: investigations of the hydrogeological conditions conducted during the Soviet and post-Soviet period (Kosolapov et al. 1993); and several recent field surveys, which mainly confirm the information from the previous investigations. The data, needed for contamination transport modeling, which were collected from representatives of industry, include concentrations of TPH in observation wells. There was no information available on initial concentration of TPH in the pond (as the pond has served as a discharge point for wastewater for over 30 years), recharge concentration of TPH (as it always depends on the load of pollutants from factories, which varies depending on the conditions of wastewater treatment systems and the capacity of the factory itself), and the characteristics of the pond, such as sedimentation properties, geometry of the pond, etc. Also, there were no opportunities to perform investigations and measurements to obtain detailed data about TPH characteristics and longitudinal dispersivity, and to identify the fraction content and degradation properties of TPH. As the constraint in data availability, particularly, detailed content of TPH in this certain case study, it was decided to follow the example from the Total Petroleum Hydrocarbon Criteria Working Group and assume that TPH is not degradable (Gustafson et al. 1997). Consequently, degradation characteristics of hydrocarbons were neglected in this study.

The study area is located on the western side of the West-Siberian plate. The surface is a mildly sloping plain with elevations ranging from 132 m above mean sea level in the southeast to 105 m in the northwest. The main recharge is from the Salair-Altai mountains, which are situated in Russia, where infiltration of precipitation, melting of glaciers, and runoff in mountain rivers generate an artesian flow toward the region. Locally, the precipitation also feeds the groundwater. The piezometric levels are established at a depth of 2-51 m below the ground surface. The values of transmissivity of the aquifer vary between 22 and 133 m^2/d, increasing in the eastern direction (Kosolapov et al. 1993). The groundwater is discharging into the Irtysh River to the west.

The hydrogeological cross-section is mainly represented by three formations (Appendix A). The formation of Upper-Quaternary deposits of the first supra flood plain terrace (aQ_{III}), which is distributed along Irtysh River, 4-5 km wide. The water-bearing sediments consist of quartz-feldspar sands. The top layer is composed of sandy loam and loam, the bottom layer is composed of gravel and pebbles. The thickness of the formation is up to 20 m. The groundwater in the aquifer has a free surface. The aquifer complex in Upper-Miocene Lower-Middle-Pliocene deposits of the Pavlodar suite ($N_{1\text{-}2}pv$) is distributed over the entire region. The thickness varies from 2-7 m in the northern and northwestern parts of the study area, and increase in a southeasterly direction to 80 m. These sediments are characterized by uneven distribution and the occurrence of sand among the clays. Water-bearing sediments in these aquifers consist of quartz-feldspar and micaceous sands. The sands are coarse-grained with gravel and pebbles in the south, and a fine-grained, sometimes clayey texture, in the north. Groundwater is mostly confined and occurs at a depth of 2-28 m to the surface. The formation of the Kulunda formation (N_2kln) is partly included in the Pavlodar formation. The thickness varies between 5 and 26 m. The water-bearing layer is characterized by alluvial sand, mixed with gravel and pebbles, with clayey and loamy lenses. The Pavlodar formation covers the Tavolzhan formation (N_1tv). This layer (N_1tv) consists mostly of clay that constitutes a bottom for the upper formation. Thus, the sediments above N_1tv formation is the subject of this study. As the formation is complex and there is only one piezometric measurement available at each well location, we only considered one layer for the modelling procedure.

2.3.2. Step 2. Groundwater modeling

The study area of this research was discretized into a 3D finite-difference model grid as a one-layer unconfined aquifer. The grid size was assumed 500 m under consideration of the large size of the territory as well as the location and the size of the potential contaminant sinks and sources. The ground surface elevation was obtained from the DEM-file from the Advanced Land Observing Satellite (ALOS) project (Advanced Land Observing Satellite (ALOS) Project). Initial head and bottom elevations of the aquifer were generated by inverse distance weighted interpolation of measured values. The groundwater levels in the observation wells around the pond were entered into the model by knowing the exact location of 18 observation wells. However, the resolution of the chosen DEM was 30×30 m, which may affect the accuracy of the calculated levels. The eastern boundary was assigned as a general head boundary, as it crosses a chain of lakes. The conductance and transmissivity values were taken from the technical reports (Panichkin et al. 2008; Kosolapov et al.1993). Irtysh River was assigned as a drain on the western boundary of the model with assigned conductance. This was calculated using:

$$C = \frac{k}{t} lw \qquad (9)$$

where k is hydraulic conductivity of riverbed material, l is length of reach, t is thickness of riverbed, and w is width of the river. The initial hydraulic conductivity values were assigned according to the existing data, and subsequently, they were calibrated during the modeling process. The southern boundary is close to the Balkyldak pond, which was the recipient of wastewater from a local chemical plant. Currently, the pond is surrounded by a concrete wall, deepened into the ground, as the pond received 10 to 15 t of mercury through wastewater from a local chemical plant up to 1990 (Ullrich et al. 2007). Hence, this boundary was defined as a no-flow boundary.

The potential recharge for shallow aquifers is normally estimated as the difference between total precipitation and evapotranspiration (Sathe and Mahanta 2019). However, the result might have a negative value, as the reported values for annual precipitation are about 303–352 mm, and for annual evaporation is around 957 mm (Heaven et al. 2007).

A steady-state condition is assumed for the model, as there is relatively negligible exploitation of groundwater resources, and there are no significant trends in observed heads during a long-term period, despite seasonal fluctuations (Radelyuk et al. 2021). The average head value was used to assign the initial head for the steady state modeling.

After calibration of the model for a regional scale assessment, the model grid was re-discretized, and the size of the grids was changed from 500 m to 100 m for local scale modeling. This modeling, firstly, gives an opportunity for a detailed estimation of particle tracking, and secondly, for insertion of an extra layer for the receiving pond, as a general-head boundary that defines lake-aquifer interactions (Mylopoulos et al. 2007). The local model was aimed to be used for following contamination transport identification. Thus, it is important to focus on a certain area, where the contaminant spread is to be estimated. Hence, a new grid was constructed, and the new model was re-run and re-calibrated.

2.3.3. Step 3. Contamination transport modeling

Pathway 1 and 2 (P1 and P2) originated from the monitoring wells W1 and W3, respectively, where coordinates x, and y, and measured concentrations of TPH were established as initial conditions (x_0=0, y_0=0, and C_0) for the contamination modeling. The W2 and W4 (for Pathways 1 and 2, respectively) are located at the boundary of the sanitary zone, where the concentration of TPH should not exceed a regulatory limit of 100 µg/L for drinking and domestic purposes according to Kazakhstani legislation (Ministry of Economy 2015). Coordinates for W2 and W4 (x, y, and dL) and measured concentrations of TPH (C) were assigned as having accurate values, while parameters T, b, p, K, α_L, α_T, and dh were given a range for the studied aquifer for running the solver coupled with the VBA code to obtain $C_{modeled}$ with a minimized error. The obtained values of transport parameters are defined as being *calibrated*. After that, the average values of the *calibrated* parameters, which are associated to the geological characteristics (b, p, K, dh) and T, as the parameter of quasi-steady conditions of the contamination, were assigned for all measurement events; and the solver was re-run to re-calibrate the model by comparison between $C_{modeled}$ and $C_{measured}$. These averages, defined as *unified*, were used for the following contaminant fate and transport modeling assessment.

The conceptual fate transport model for P1 and P2, on the examples of lines BD and BC, respectively, is presented in Figure 2. The directions towards the nearest agricultural fields were chosen, as the nearest consumers of groundwater. The results for P1 are expected having a wave structure as the distance for them was calculated along the example of the direction BD in Figure 2. This means that y-coordinates were moved in the negative direction, which caused higher concentrations with the following cross-section and y=0, and subsequently heading away from the source of the pollution. The direction BC in Figure 2 indicates P2 with a straightforward direction from the source of pollution. The distance was modeled until the concentration of TPH reached a concentration that complied with the regulatory limit. The distance (dL_i), and related dh_i steps were assumed based on the groundwater model.

The final step was to look at the sensitivity of the parameters. The idea of this analysis is to identify the most critical parameters for that influence the calibration of the contaminant fate and transport model. The parameters *K*, *T*, *b*, *p*, *dh*, α_L, and α_T were assessed, as input parameters for solving Eqn. (3). The assessment was performed by individually varying only one parameter at the time within its range of possible values.

Parameter uncertainty is always a major concern. But the purpose of this study was to provide a tool that gives a general picture of contamination transport by illustrating the patterns of change in contaminant concentration in space with the following assessment for potential fate for the environment and local inhabitants. Calibration, validation, and sensitivity analysis of the model were done to the extent when available data allowed for this, while a detailed discussion about this procedure including uncertainty analysis is beyond the scope of this study (McMahon et al. 2001).

3. Results and Discussion

3.1. Groundwater modelling

The hydraulic conductivity, conductance of boundaries, and drainage characteristics of the river were calibrated using PEST and PEST Pilot points after the initial forward run of MODFLOW (Fig. 3a). The simulated hydraulic heads were compared to observed heads (Appendix B). The RMSE was equal to 0.7 m and the R^2 coefficient equal to 0.96, which indicate good performance of the model.

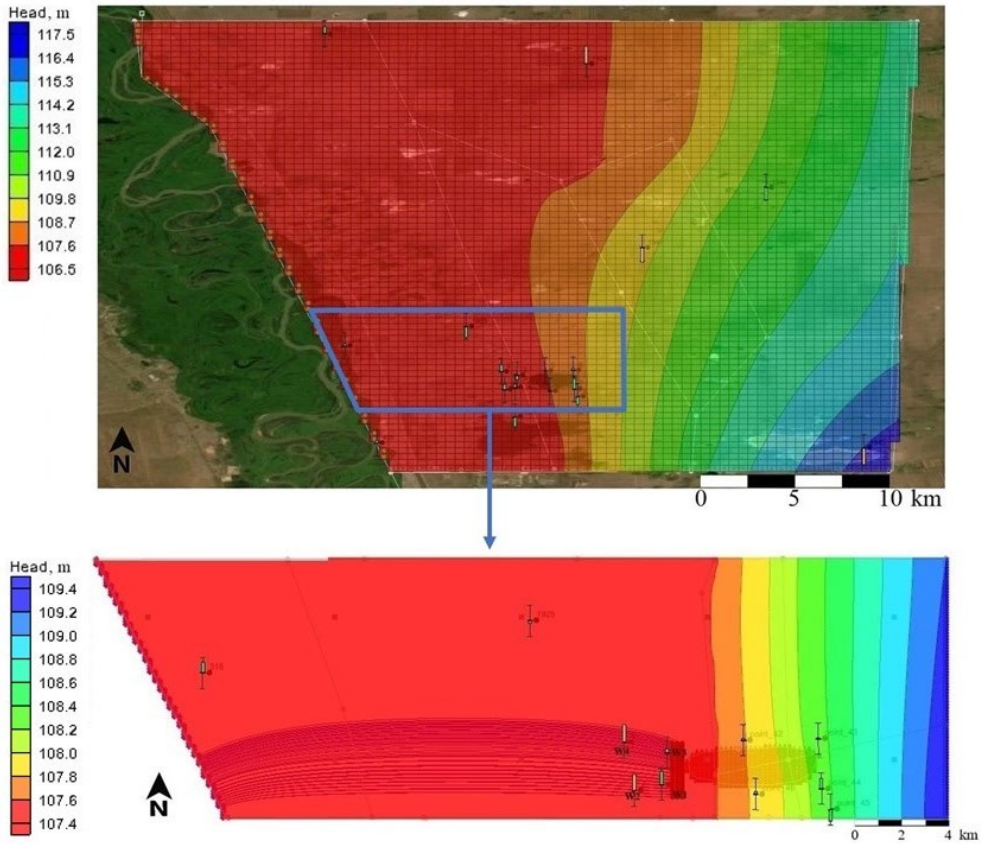


Figure 3. *Regional (a) and local (b) scale groundwater model.*

The results of the calibration reflect the lithology of the study area (Appendix C). The higher hydraulic conductivity values (5.5 m/d) occur in sediments adjacent to the Irtysh River and in Upper-Quaternary deposits (aQ_{III}), as they consist mainly of well sorted quartz-feldspar rich sands and gravels. The decrease of hydraulic conductivity (5.5-0.8 m/d) from the northwest to the southeast is explained by the local topography, as the groundwater is deeper, and extent of covered (confined) conditions of the aquifer is larger. The conductance of the drain (river) (50 m^2/d) and transmissivity of the boundaries (125 m^2/d) were approximately equal to the accessible data (from technical reports) after calibration, which confirms an acceptable estimation of groundwater flow.

After calibration and adjustment of the regional model, local scale modeling using MODFLOW and MODPATH was performed. Figure 3b shows the simulated water level contours for the steady-state conditions. This suggests that the direction of groundwater flow and contaminant transport would be in a westerly direction with some displacement towards the southwest. Wells 1 and 2 (W1 and W2) and Wells 3 and 4 (W3 and W4) could be used for contamination transport modeling, as they are in the downstream direction from the source. Particle tracking showed the potential transport of contaminants towards agricultural fields, where groundwater is used for irrigation (4.5 km from the pond) and nearby rural areas (Michurino and Pavlodarskoe villages, 8 km from the pond). However, MODPATH considers only porosity and not longitudinal dispersivity. The RMSE of the local model was equal to 0.6 m and the R^2 coefficient equal to 0.68, which show a good fit of the model (Appendix D).

3.2. Contamination transport modeling

After calibration of the groundwater model, two pathways, located downstream from the source of pollution, were chosen for the contamination transport modeling. Figure 4 and Appendix E show the results of the calibration of the transport parameters. The R^2 coefficient was equal to 0.9 that indicates the good performance of the model. The calculated means of the differences between groundwater levels (*dh*) by MODFLOW were equal to 0.1 m and match the contamination transport model results. However, *dh* is one of the most uncertain parameters in this case study, as the number of measurements of groundwater level is low.

The assumptions are considered credible if *Q* (from Eqn. (5)) is similar in both models. In the present case, the average flow rate was calculated to be 50 m^3/d and the same value resulted from the contamination transport model. The large plume width (*T*) is explained by the width of the Sarymsaq pond, which is equal to 1.5 km. Hence, according to dispersion, *T* might be larger than 1500 m. The longitudinal dispersivity depends on the scale of spread of contamination and was close to values found in literature. However, both parameters had high range of potential values, caused by a large scale of calculations. Further studies on a smaller scale may give more accurate results. The calibrated values of aquifer thickness were equal to 10 m, which is confirmed by local lithology (Appendix A). The range for hydraulic conductivity and porosity was extracted from literature and was given as 0.8-8 m/d and 0.22-0.3, respectively. The unified values were equal to 5.6 m/d and 0.28, for hydraulic conductivity and porosity, respectively.

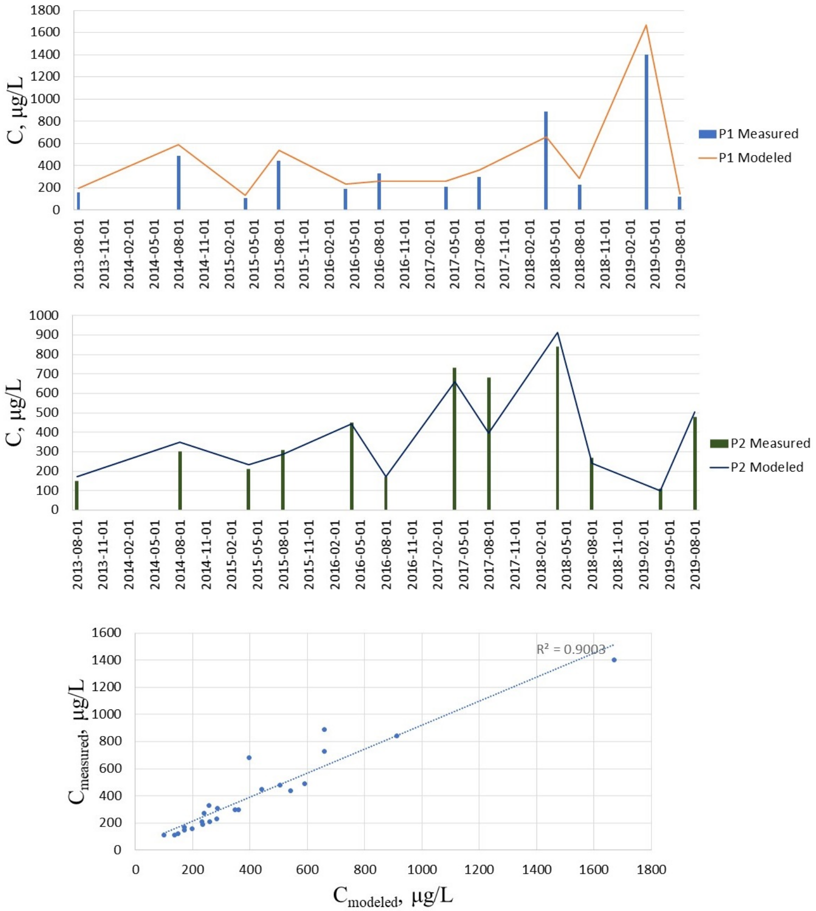


Figure 4. *Results of transport contamination model using unified values of the parameters.*

Figure 5 presents the potential results of the contamination transport, based on measured concentrations in the monitoring wells, and unified transport geological parameters for individual cases and historical scenarios. The distance (dL_i) step was assumed as the square root of x+100 and y+20 m from the observation points. The dh_i was estimated as 0.01 m for each dL_i step, based on the groundwater model. Obviously, the plume width correlates with the starting concentrations. The potential maximum distribution during the spring season in 2019 and 2018 was equal to 6 and 3 km for Pathways 1 and 2, respectively. The starting concentrations (C_0) showed maximum historical values in those years. The same situation was found for the autumn periods when the potential maximum spreading of the contamination was 4.5 and 2.6 km for Pathways 1 and 2, respectively. The calculated distance is higher during the spring seasons than in autumn. Lower values of the calculated plume fit the lower concentrations with a resulting shorter distance from the origin of pollution. However, even for these cases, the distance was relatively large, almost 1.2 km from the source of the contamination.

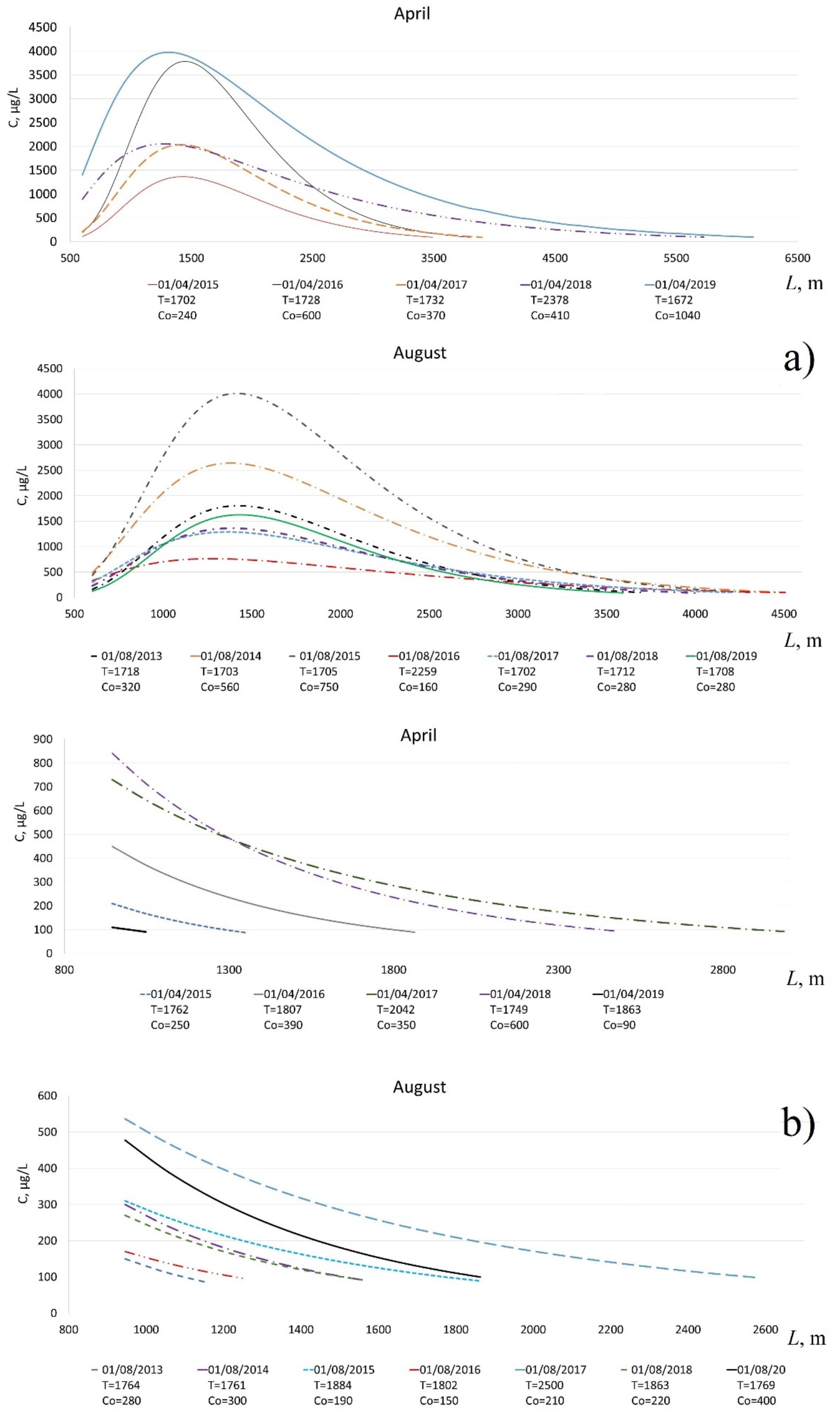
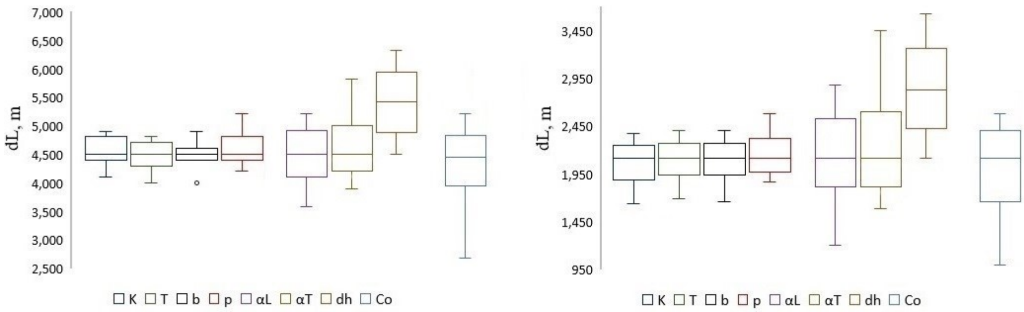


Figure 5. *Modeled contamination depending on distance from a) W1 and b) W3.*

The final step of the application is the analysis of the sensitivity of aquifer parameters. The ranges for K, T, b, and p were changed several times in an equal manner: they were decreased by 25 % and 50 % and increased by 25 % and 50 %. For the investigation of the relationships between dh and dL_i, the range for dh was considered between 0.01 and 0.1 m. The C_0 was assumed to be 500 µg/L for all scenarios. To assess the potential spread of plume, depending on the initial load of the TPH, the range for C_0 was considered between 50 and 1000 µg/L. After establishing new values, dL_i was calculated to the extent, when the concentration of TPH is within permissible levels. The results are presented in Figure 6. While all parameters show relevant changes in the resulting dL_i within the range of change, longitudinal and transverse dynamic dispersivity together with plume width were considered as the most sensitive parameters in this study. This is explained by the fact that these parameters might be changed over time depending on contamination characteristics, while parameters describing geological characteristics are constant. The increase of dh causes significant increase in the distance of plume spreading, as it is related to the enhanced linear velocity, and consequently, enhanced injection rate of the contaminant. The parameters may vary significantly depending on the scale and characteristics of contaminants. If the C_0 is equal to 1000 µg/L, the contamination can spread up to 5 km for Pathway 1 and 2.5 km for Pathway 2. The highest rate of the spreading belongs to the area near the source of pollution, e.g., the growth of the starting concentrations from 100 to 150 µg/L causes extension of the plume spread corresponding to 0.25 km (from 1.30 to 1.55 km) for Pathway 2, while the following dL_i was changed for 120-50 m for each 50 µg/L. Thus, future data acquisition for the most sensitive parameters is required to better control the situation of the groundwater contamination in the region.



a) b)

Figure 6. *Sensitivity analysis for a) Pathway 1 and b) Pathway 2.*

4. Conclusions

The management and remediation of groundwater contamination in developing countries is often hampered by lack of data. In this case, it is possible to assess the potential contamination from a holistic viewpoint with some general results, which can be beneficial for guiding future investigations. The method presented in this study has several advantages and is proposed as an example for cases where detailed site-specific data are not available. Basic information about the local hydrogeology and concentrations of pollutants at observation points can be used to estimate the further spreading of pollution. When calculated errors from contamination transport modeling and subsequently calibrated parameters, related to local conditions characteristics (i.e., T, b, K, and dh), match or confirm the results of the calibrated MODFLOW model and available literature data, the model can be considered to be reliable. At the same time, incorrect identification of important parameters, such as initial coordinates, increases the risks of incorrect modeling. Also, the lack of knowledge about contaminant characteristics affects the study. The processes of volatilization and degradation, which are not considered in this study, decrease the amount of petroleum compounds in space and time. However, some petroleum compounds may not be degradable, which cause risks even at low concentrations.

This study showed that the risks for inhabitants in the potentially affected rural area of Kazakhstan can be avoided, as the plume has not reached the villages considered to be within the risk zone. However, agricultural areas at a distance of 2-6 km downstream the source of pollution could be affected by contaminated groundwater. Thus, the recommendation is to avoid usage of groundwater from the shallow aquifer for irrigation purposes in this area. The authors suggest performing additional investigations to determine the extent to which the TPH plume has spread from the contamination source, based on the general results, and especially the results of the sensitivity analysis. This study has also shown the need for local industries to pre-treat wastewater properly before discharging to ponds to decrease the potential fate and spreading of the pollution to the subsurface.

Finally, this study highlights the necessity of integrating key stakeholders in the government-science-industry collaboration. The joint effect of governmental activities, scientific approach, and industrial activity can contribute to the reduction of negative societal impact of pollution release.

CRediT authorship contribution statement

Ivan Radelyuk: Conceptualization, Methodology, Formal analysis, Funding acquisition, Investigation, Data Curation, Writing - Original Draft, Writing - Review & Editing. **Mehran Naseri-Rad**: Conceptualization, Methodology, Software, Formal analysis, Writing - Original Draft, Writing - Review & Editing. **Hossein Hashemi**: Conceptualization, Methodology, Resources, Supervision, Writing - Review & Editing. **Magnus Persson**: Conceptualization, Supervision, Writing - Review & Editing. **Ronny Berndtsson**: Supervision, Writing - Review & Editing. **Madeniyet Yelubay**: Data Curation, Investigation. **Kamshat Tussupova**: Conceptualization, Writing - Review & Editing.

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Conflict of interest. The authors declare that they have no conflicts of interest regarding the publication of this paper.

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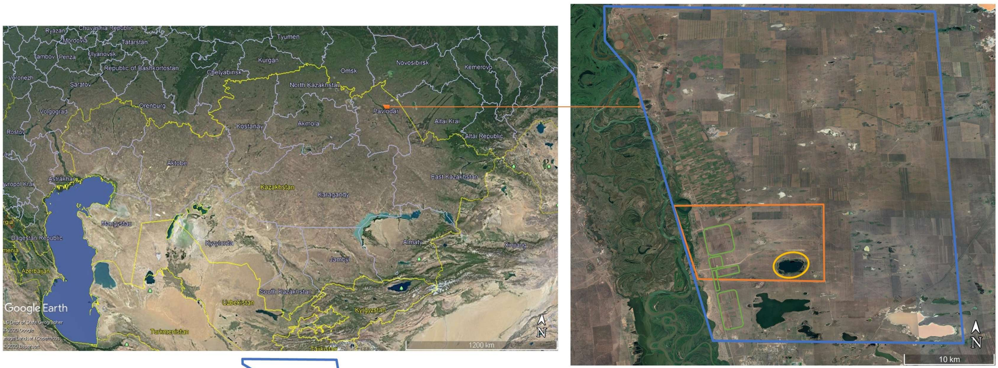
Appendix A. Location and lithology (Kosolapov et al. 1993) of the study area in Kazakhstan.

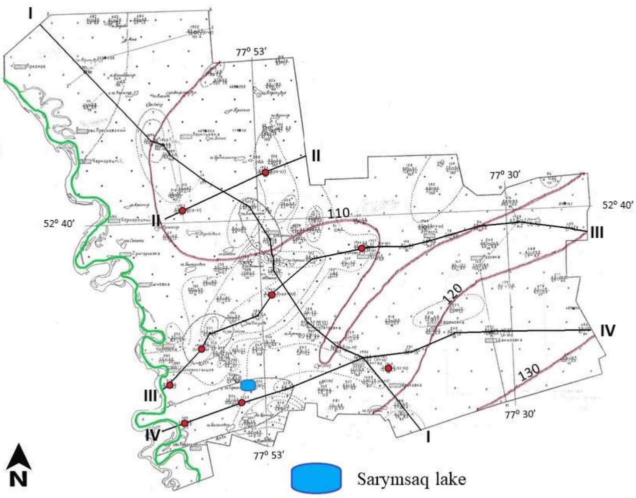


Regional scale boundaries

Local scale boundaries

Agricultural fields

Sarymsaq



Cross-sections (I-IV) on the selected region

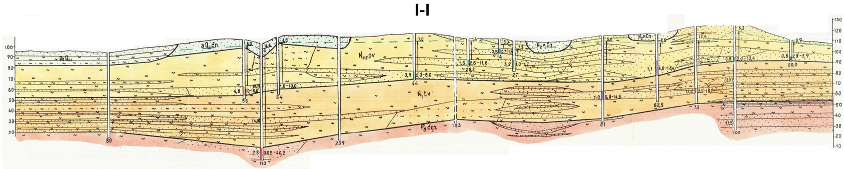
River contour

Sarymsaq lake

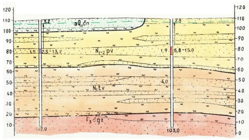
130 Piezometric lines with groundwater level value

Boreholes

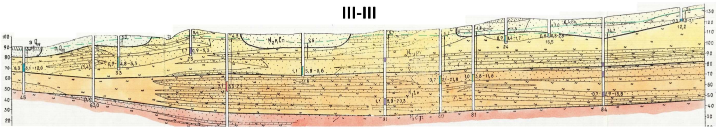
I-I



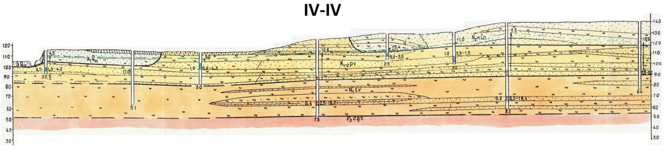
II-II

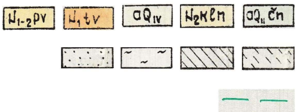


III-III



IV-IV





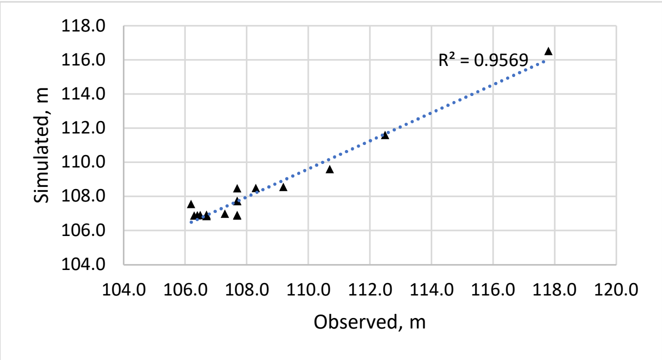
- formations

- soil types (sand, clay, loam, sandy loam)

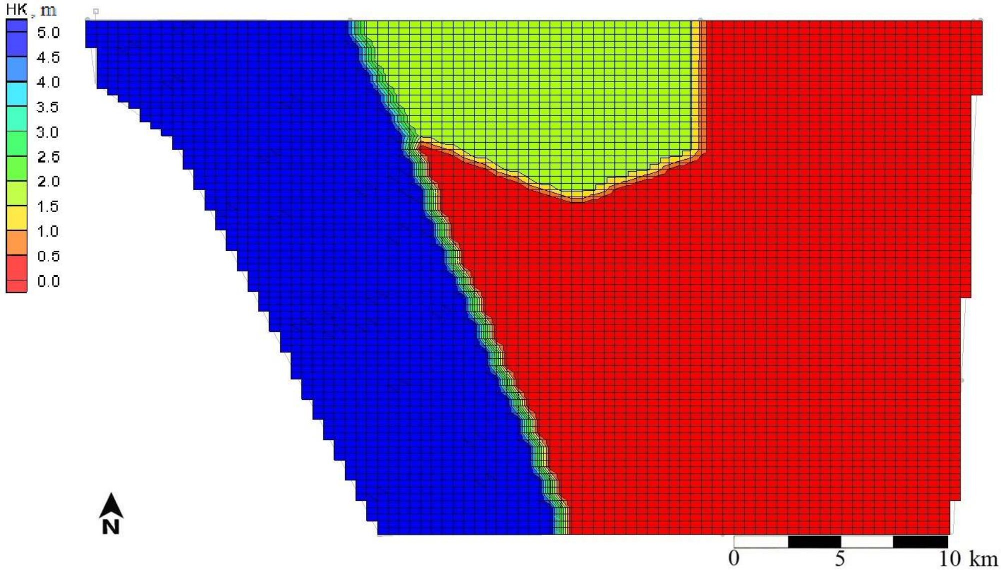
- groundwater level

Appendix B. Scatter plot of modelled versus observed head. Regional scale.

№	Well ID	Observed Head, m	Simulated Head, m	Residual Head, m
1	1944	112.5	111.6	0.91
2	1947	110.7	109.6	1.11
3	1924	106.2	107.6	-1.35
4	1923	106.3	106.9	-0.58
5	316	106.7	106.8	-0.14
6	405	106.7	106.9	-0.16
7	1929	107.7	106.9	0.79
8	1925	107.7	106.9	0.82
9	1945	117.8	116.5	1.28
10	1	106.7	106.9	-0.22
11	2	106.5	106.9	-0.40
12	3	107.3	107.0	0.32
13	4	106.4	106.9	-0.50
14	5	107.7	107.7	-0.02
15	6	108.3	108.5	-0.19
16	7	107.7	108.5	-0.78
17	8	109.2	108.6	0.64
18	9	107.7	107.7	-0.03

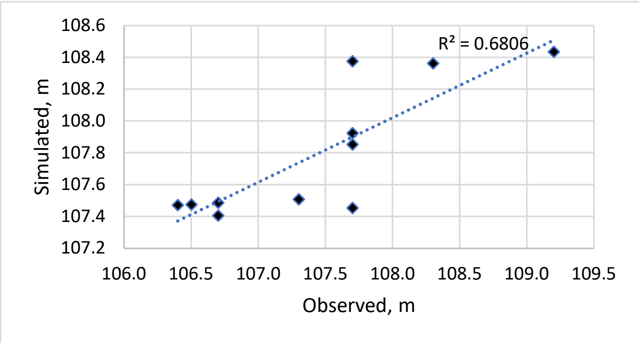


Appendix C. Calibrated HK values.



Appendix D. Difference between calculated and observed head. Local scale.

№	Well ID	Observed Head, m	Simulated Head, m	Residual Head, m
1	316	106.7	107.4	-0.71
2	1925	107.7	107.5	0.25
3	1	106.7	107.5	-0.79
4	2	106.5	107.5	-0.98
5	3	107.3	107.5	-0.21
6	4	106.4	107.5	-1.07
7	5	107.7	107.9	-0.15
8	6	108.3	108.4	-0.06
9	7	107.7	108.4	-0.68
10	8	109.2	108.4	0.76
11	9	107.7	107.9	-0.23



Appendix E. Unified results of transport contamination model after calibration.

	X, m	Y, m	Co (µg/L)	Q (m^3/d)	T, m	b, m	Mass Rate	K (m/d)	p	dh (m)	dL (m)	Vx (m/d)	αL (m)	Coef.	αT (m)	DL	DT	Modeled (µg/L)	Measured (µg/L)	Error (µg/L)
Pathway 1:	569.7	193.6	320	61.9	1845	10	1979.9	5.61	0.28	0.10	602.1	0.0034	50.97	9.63	5.29	0.17	0.02	196.8	160	36.8
			560	61.6			3447.9			0.10		0.0033	54.65	7.24	7.54	0.18	0.03	589.9	490	99.9
			240	63.4			1522.4			0.10		0.0034	50.03	9.90	5.06	0.17	0.02	135.3	110	25.3
			750	61.9			4640.1			0.10		0.0034	50.96	8.76	5.81	0.17	0.02	541.1	440	101.1
			600	61.7			3699.5			0.10		0.0033	50.46	12.01	4.20	0.17	0.01	233.7	190	43.7
			160	58.6			936.9			0.09		0.0032	69.81	6.01	11.61	0.22	0.04	256.5	330	73.5
			370	65.4			2421.0			0.11		0.0036	51.80	9.11	5.69	0.18	0.02	258.3	210	48.3
			290	61.9			1793.8			0.10		0.0034	58.79	6.76	8.69	0.20	0.03	360.7	300	60.7
			410	63.1			2588.5			0.10		0.0034	69.85	6.01	11.63	0.24	0.04	658.1	890	231.9
			280	61.7			1728.1			0.10		0.0034	54.80	7.52	7.29	0.18	0.02	282.9	230	52.9
			1040	60.1			6249.5			0.10		0.0033	69.91	6.01	11.64	0.23	0.04	1670.0	1400	270.0
			280	63.5			1777.5			0.10		0.0034	50.08	10.27	4.88	0.17	0.02	147.6	120	27.6
Pathway 2:	923.0	206.4	280	20.4			571.8			0.05	945.8	0.0011	68.34	17.42	3.92	0.08	0.00	170.6	150	20.6
			300	36.2			1086.2			0.09		0.0020	73.20	11.87	6.17	0.14	0.01	347.3	300	47.3
			250	36.9			921.4			0.09		0.0020	69.38	13.51	5.13	0.14	0.01	231.1	210	21.1
			190	39.6			753.2			0.10		0.0022	71.41	8.63	8.27	0.15	0.02	286.3	310	23.7
			390	33.4			1301.9			0.08		0.0018	73.12	12.10	6.04	0.13	0.01	441.7	450	8.3
			150	48.0			719.9			0.12		0.0026	68.77	11.35	6.06	0.18	0.02	169.7	170	0.3
			350	37.6			1317.1			0.10		0.0020	75.00	6.00	12.50	0.15	0.03	659.4	730	70.6
			210	4.1			86.4			0.01		0.0002	75.00	6.00	12.50	0.02	0.00	395.6	680	284.4
			600	29.9			1793.7			0.08		0.0016	61.20	7.28	8.40	0.10	0.01	912.3	840	72.3
			220	42.2			929.2			0.11		0.0023	70.72	12.06	5.86	0.16	0.01	240.2	270	29.8
			90	39.6			356.1			0.10		0.0021	69.26	11.78	5.88	0.15	0.01	98.5	110	11.6
			400	33.8			1351.2			0.09		0.0018	64.85	9.63	6.74	0.12	0.01	503.7	480	23.7

Paper IV

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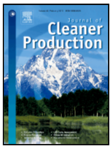

Oil Refinery and Water Pollution in the Context of Sustainable Development: Developing and Developed countries

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ABSTRACT

This paper is an attempt to evaluate the impact of the oil refinery industry on water resources worldwide from the point of view of sustainable development (SD). The local laws, reports from the industry and environmental agencies, conditions of the final disposal system were analysed. Key aspects, such as existing approaches for treatment systems, quality of treated wastewater, and ways to assure the safety of them were compared. The comparison between industrialised (represented by the USA and EU) and developing countries (Kazakhstan used as an example) shows that several obstacles, such as loopholes in legislation, historical contamination, and miscommunicating between stakeholders, exist, despite the formal promotion of the SD concept. That policy should be implemented based on the relevant scientific investigation through the possibility of integrating the respective technological development, an adequate system of environmental impact assessment, and fair operational monitoring.

1. Introduction

Sustainable Development (SD) has become an ideology, which builds a modern world. The 2030 Agenda for Sustainable Development calls all people, from individuals to crucial stakeholders, businesspersons and international organisations, to take actions for solving the current challenges formulated in Sustainable Development Goals (SDGs) (UN 2015). One of the common definitions of Sustainable Development is "Enhancing quality of life and thus allowing people to live in a healthy environment and improve social, economic and environmental conditions for present and future generations" (Ortiz et al., 2009). From a certain point of view, "Sustainable" means "Responsible". Any current suggestion, decision, or action on any level should be based on the concept, which supports not only immediate benefits but to ensure equal rights of all types of benefits, including well-being and a healthy environment, for future generations.

Relationships between SD and industry have been complicated. It can be clearly presented within related Sustainable Development Goals (SDGs). When one of the elements does not work, it affects the success of the other goals. An example is presented in Fig. 1. Any type of industry is related to several SDGs (Appendix A). SDGs 8, 9, 12 and 13 are directly connected with the industrial processes. The processes should be innovative to achieve rational and efficient resource use (SDGs 8, 9, 12) and eliminate impact on the environment through sufficient treatment systems, which lead to the deceleration of climate change (SDG 13). The SDG 6 "Clean Water and Sanitation" requires: (i) to eliminate potential hazards of disposal of effluents; (ii) to adopt water-saving techniques to reduce the consumption of fresh water to address water scarcity (Jia et al., 2020); and, (iii) protect water-related ecosystems, including rivers, lakes and aquifers. The SDG 14 "Life below Water" specifically focuses on the consequences of any kind of pollution for the aquatic world. Environment (water, soil and air) impacts the health of people, which belongs to SDGs 3 and 11. If the industry neglects principles of responsibility during the production process, it might lead to the crash of the "sustainability" system: deteriorated ecosystems and unhealthy people, locally or globally. The Agenda considers the involvement of all countries and their cooperation (SDG 17).

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Fig. 1. SDGs related to the industry (Source: the authors).

UN has encouraged parliaments and lawmakers to implement SDGs as national ideas via suitable law-making, scientific and innovative technological approach, and suitable control (UNDP 2016).

The concept of "Sustainable water use" (SWU) brings several SDGs related to the water together. The SWU aims to assure three pillars of sustainability: social, environmental, and economical. Sustainable water use in the industrial context covers several factors of three dimensions of SD and their interactions, as shown in Fig. 2. Economic factors are represented by the processes inside the industry. The industry uses technologies to treat supplied and processed water and to utilise it in a safe manner. These technologies are associated with respective cost (Baleta et al., 2019). Environmental factors consider water quality in water sources and wastewater recipients. Interactions between economic and environmental factors are characterised by attempts to decrease the impact of industrial activities on water bodies and make water viable for following consumers by the usage of efficient technologies. Social factors are represented by ensuring public safety (e.g., health) and mainly regulated by the government. The governmental and civic authorities should ensure the availability of safe water by appropriate legislative and environmental tools (Hjorth and Madani 2014). Economic and social factors should be met by establishing the idea of equal rights for different water users. Appropriate legislation ensures the responsibility of the industry to apply related efficient and water-saving technologies.

Implementation of the SWU is important for two reasons. First, water consumption by industry ranges between 10% and 57% of total water consumption in different countries (Voulvoulis 2018). Second, industrial activities are recognised as one of the major sources of water pollution worldwide and can be quantified by environmental footprints (Čuček et al., 2012). The developing countries face challenges towards the implementation of the SWU. This type of countries is characterised by applying efforts to diversify the economy from just exporting resources to build advanced technological infrastructure. This process includes accelerated industrialisation and growth of already existed manufacturing capacity, which increase the pressure on water resources in both an increase in water consumption and the needs for a decrease in water pollution (Naseri-Rad et al., 2020).

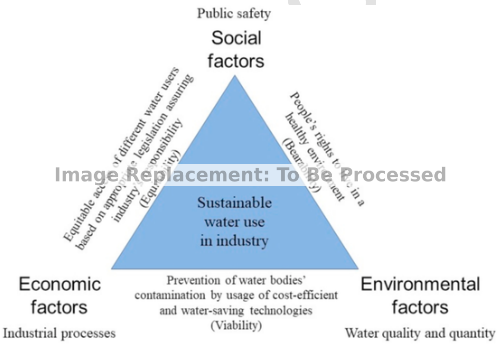

Fig. 2. The framework of Sustainable water use in industry (Source: the authors).

This research aims to compare strategies and efficiency of the implementation of the SWU system in industry between developed (represented by the EU and the USA) and developing (Kazakhstan used as an example) countries. Specific type of industry – the oil refinery sector was chosen as a case study. According to the BP Statistical Review, the USA and EU hold the maximal capacity of oil refining units worldwide (BP, 2019). The western world has a reputation as drivers and promoters of sustainable development. SDG 8.4 clearly states that the developed countries are aimed to lead and transfer their experience in "global resource efficiency in consumption and production and endeavour to decouple economic growth from environmental degradation". According to a UN "World Economic Situation and Prospects 2019" book, Kazakhstan has been rated as a fuel-exporting country with transitional from developing to the developed economy (UN 2019). According to the Environmental Performance Review for Kazakhstan (UNECE 2019), the oil refinery cluster in Kazakhstan is one of the biggest sources of water contamination. Thus, the authors are interested in looking at how refinery companies deal with Sustainable Water Use. This paper discusses the engagement of all key stakeholders, such as government, industry, and academy, into a dialogue towards SD.

While the previous publication aimed to investigate the experience of the legislation of different countries and applied wastewater treatment techniques (Radelyuk et al., 2019); this paper mostly focuses on the interrelations and synergies between the oil refinery industry and water pollution with the focus on the problems of potential fate on affected water bodies in the context of SD.

2. Methodology

The DPSIR (Drivers-Pressures-State-Impact-Response) framework has been proposed by a Guidance document from the EU to analyse the existing pressures and their impacts on water resources (EU 2002). Accordingly, this study implements the DPSIR concept, as is shown in Fig. 3. Principles of the SWU have become the drivers to meet socio-environmental awareness and to decrease the *pressure* on water resources. The hypothesis is that *pressure* is caused by improper wastewater treatment. The resulting *state* or indicator of the *pressure* (which is usually measurable, according to the DPSIR approach) can show high concentrations of the contaminants in the wastewater, and consequently, in the recipient. The *impact* may differ, including deteriorated or destroyed ecosystems, unsafe drinking water, or the waste of water in the regions where water scarcity exists. The measures are taken to improve the *state*, and the *response* has to address the identified pressures.

The structure of the performed assessment is presented in Fig. 4. The authors aimed to analyse available "first-hand" information about the *state* and the *impact* of governmental bodies. This information included legislative documents, such as laws, orders, reports, and standards; documents and reports from responsible authorities, such as En-

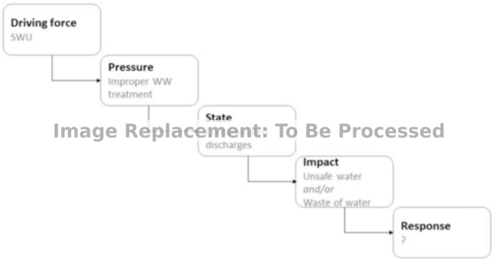

Fig. 3. The DPSIR framework for this study (Source: the authors).

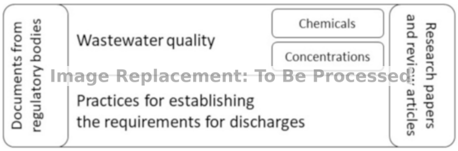

Fig. 4. Searching methodology: a conceptual framework (Source: the authors).

vironmental Protection Agencies and oil refinery operators, and statistical datasets. The limitations for consideration of the *state and impact* information as relevant were 1) existing effluents conditions, including a description of the contaminants and their concentrations, and 2) description of characteristics of wastewater recipients. Also, the authors aimed to identify the pros and cons of the applied *response* for the establishing of current criteria. An extended literature review was carried out, despite the analysis of official information. The authors also attempted to overview the relevant experience of the SWU implementation (as *drivers*) in relevant scientific publications. The above criteria were used for consideration of the relevance of the reviewed literature. Highly cited papers in peer-reviewed journals were examined with the following “snowball sampling” review using the Scopus database. A combination of keywords (refinery AND (effluents OR wastewater OR waste AND water)) resulted in 1148 publications. 36 publications were chosen as sound examples of the respective research-supported solutions for decision-makers toward the SWU in the oil refinery sector. Consideration did not include the publications about treatment methods, as the previous publication from the authors already investigated the issue.

This paper consists of the Results, Discussion, and Conclusions sections. The Results section consists of three sub-sections, where the findings for the USA, the EU, and Kazakhstan are presented. The structure of the sub-section is as following:

(i) Description of historical background in legislative standards and oil refinery industry.
(ii) Description of current industry conditions with particular attention on wastewater treatment units.
(iii) Description of wastewater characteristics.
(iv) Description of wastewater recipients and potential consequences for the environment.

3. Resulting observations

The authors identified strategies from three selected regions, which have a goal to achieve a sustainable and safe environment via establishing the criteria for maximum allowable concentrations of contaminants in wastewater. The USA applies the National Pollutant Discharge Elimination System (NPDES), the EU uses the system of Whole Effluent Assessment (WEA), and Kazakhstan uses the Environmental Impact Assessment (EIA). The authors firstly investigated those approaches in each region – which actions are considered under the decision-making systems; and secondly, discussed their strengths and weaknesses (Fig. 5).

3.1. The USA observation

The history of regulatory relationships between the USA Environmental Protection Agency (EPA) and oil refinery effluents systems started in 1974 with the promulgation of effluent limitations guidelines and standards (ELGs). This document was applied to establish pretreatment standards for existing and new sources of pollution with the permissible concentrations of few pollutants, such as ammonia, oil and grease, biochemical oxygen demand (BOD), phenolic compounds, sulfides and chromium in the effluents (USEPA 1974). The guidelines had been constantly revised, with the final document accepted in 1985. This resulted in more strict criteria for treatment standards and application of innovative Best Available Technologies Economically Achievable (BAT) (USEPA 1985). The permanent monitoring of available enhancements in technological and scientific progress enabled to enhance the efficiency of the law through the following amendments.

Implementation of BAT became one of the leading factors, which makes this guideline efficient to protect the environment towards the elimination of the discharge of all pollutants (in the USA) (U.S.Code). The principle of BAT is to find the most efficient and cheapest way to meet the requirements for local ecosphere safety by reduction or elimination of pollution. The idea of implementation of BAT is to invest in the prevention of contamination instead of pollution and consequent remediation actions.

One more of the special characteristics of the guidelines is using “in-plant” and “end-of-pipe” technologies. “In-plant” system controls the amount of pollutants in processing water after each technological unit through preliminary treatment methods, such as separation of stormwater and processed water; sour water strippers; or through re-using water, e.g. for using lightly contaminated water in water cooling towers. This approach reduces the burden on the final (or “end-of-pipe”) treatment system and enhances the efficiency of it. “End-of-pipe” technology assumes deep wastewater treatment and aims to eliminate or significantly reduce the concentration of pollutants in final effluents. Advanced treatment techniques for the oil refinery industry were described in detail in the previous publication from the authors (Radelyuk et al., 2019). They can include, e.g.:

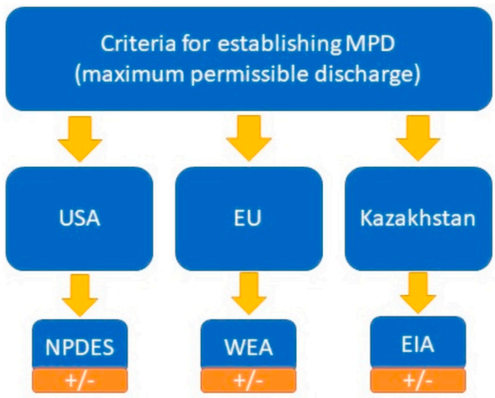

Fig. 5. Conceptual framework of performed observations (Source: the authors).

(i) Combination of different pretreatment units (electrocoagulation-flocculation, dissolved air flotation (DAF), oil traps, etc.)
(ii) Enhanced common secondary treatment methods (e.g. activated sludge coupled with oxidation ponds, trickling filters, moving bed biofilm reactors (MBBR), etc.).
(iii) Polishing approached (wetlands, advanced oxidation processes, membrane technologies).

Under the regulation of principles of BAT and "end-of-pipe" and "in-plant" technologies, the EPA establishes production-based mass limitations for the pollutants included in the ELG. The main source of pollution is the desalination unit of the refinery, coupled with the atmospheric distillation unit. Crude oil contains a high level of sulfur, salts and metals. The desalination unit removes a major amount of salts by emulsifiers and generates 3–10 vol% on a crude charge into wastewater flow (Alva-Argaez et al., 2007). A significant amount of sulfides, ammonia, phenols, oil, chlorides and mercaptans comes after the distillation process. These chemicals are included in the list of priority pollutants for the refinery industry with the main focus on crude oil, or it is called "petroleum hydrocarbons". While thousands of hydrocarbons exist, only very a few of them are investigated in detail (WHO 2008). Hydrocarbons are assumed as toxic substances, while the hazard level ranges between different groups of them. There is no unified way for associated terminology of the hydrocarbons related to industrial wastewater discharges yet. Depending on the focus contaminants, phase conditions, type of analysis, etc., the petroleum hydrocarbons in different regions are called TPH (total petroleum hydrocarbons), Oil in Water (OiW), or Oil and Grease.

The EPA regularly conducts a study of wastewater discharges from petroleum refineries to assess the situation in the sector. The evaluation includes 1) study visits, 2)questionnaire of the petroleum refineries to request information about their water use processes, crude processed, production rates, unit operations, wastewater characteristics, pollution prevention, and wastewater management, treatment, and discharge, and 3) data extraction from the national systems of Discharge Monitoring Report (DMR) and Toxics Release Inventory (TRI).

Recent reviews of 2011 and 2014 concluded that the regulations should be changed due to new information, such as reported discharges of toxic compounds, such as dioxin and dioxin-like compounds, polycyclic aromatic compounds (PACs) and increase of refineries reporting metals discharges, instead of only chromium included in the current guideline (USEPA 2019).

The system of establishing the requirements for each case of pollution, titled National Pollutant Discharge Elimination System (NPDES), includes several investigations (USEPA 2010). Firstly, limitations are based on the capabilities of the technologies available to control those discharges. Industrial processes and raw materials, facility size, geographical location, and age of facility and equipment are considered. Secondly, water quality-based effluent limitations are calculated. The conditions of the water body, which receives the discharges, are assessed for background contamination. Parameter-Specific Approach, Whole Effluent Toxicity (WET) Approach, and Bioassessment Approach are used in this step. Parameter-specific involves a site-specific assessment of the proposed discharge and its potential effect on the receiving water. The WET test is used to establish the frameworks of permits. This test measures the exposure of the contamination to the conditions of living of the selected organisms, which serve as "indicators" of their ability to live with the level of the contamination. The criteria approach is used to assess the overall biological integrity of an aquatic community. The idea is to finally establish the level to the extent when nature can utilise the hazard in its own functions.

The authors used the latest study report (USEPA 2019) as a basement for the following investigation. This report has presented information about 143 refineries in the USA. The authors focused on the category of refineries, which discharge their effluents directly into the environment to evaluate the consequent potential effect.

Table 1 shows that only 20 of 143 refineries send their pre-treated effluents into the municipal wastewater collection systems. Twelve refineries are defined as unknown and excluded from consideration. Two refineries (Evanston Refinery and Sinclair Refinery) are defined with the "Zero Discharge" status. It means they achieved the possibility of near-zero liquid discharge through the full water reuse (Koppol et al., 2004), which seems to be an ideal case for the elimination of risks.

90 refineries with direct discharges, coupled with nine refineries with both types of discharges, are subjects of investigation for this study (Table 2). Wastewater treatment of more than half of refineries is characterised by "Biological treatment". It means that they commonly use primary and secondary oil/water separation units, coupled with one of the types of biological treatment techniques. The type of biological treatment varies widely, from the basic activated sludge to advanced, such as MBBR, membrane bioreactor (MBR), ADVENT integral biological system, etc. Refineries, categorised as "Current BAT technologies" (23 of 99), use an extra unit after a step of biological treatment to achieve the final requirements of the NPDES. Generally (16 of 23), it is a filtration implementation whenever the other refineries use settling ponds, extra aeration, and chemical oxidation. Five refineries use the most advanced wastewater treatment techniques and implemented more than one extra unit for polishing. Ion exchange, selenium reduction plant, and Filtration and Polishing identify those technologies as "Beyond BAT technologies".

The EPA identified 26 primary pollutants for monitoring in the refinery effluents. The reasons for the inclusion of the chosen substances were their presence in the untreated refining process wastewater and their rate of toxicity. Appendix B presents annual mean concentrations and estimated loadings of contaminants included in the list of pollutants. The EPA has tried to estimate the amount of the pollutants of interest in the discharges as average concentrations and their annual loading. The criteria for inclusion was the refineries, which directly discharge the treated wastewater into the surface water. That estimation has a limitation of data availability. For example, only three refineries provided data about BTEX (benzene, toluene, ethylbenzene, xylene) in their wastewater, or there is no reported data for polycyclic aromatic hydrocarbons (PAHs).

While the reported amounts of pollutants seem to be a significant contribution to water pollution, the averaged and simplified estimation does not show a detailed picture. The authors investigated the charac-

Table 1
US refineries by discharge status (USEPA 2019).

Discharge Status	Number of Refineries
Direct	90
Indirect	30
Direct & Indirect	9
Zero Discharge	2
Unknown	12
Total	**143**

Table 2
Categorisation by treatment methodology (USEPA 2019).

Categorisation by treatment approaches	Number of refineries
Biological treatment	56
Current BAT technologies	23
Beyond BAT technologies	5
Treatment other than Biological Treatment	7
No data/No information available	8
Total	**99**

teristics of the refineries wastewater at Top-20 refineries by their operating capacity, which practice direct discharges. Appendix C represents the searching methodology used by the authors. The authors used available DMR and TRI data from the online Water Pollutant Loading Tool. The data of monitoring for the year 2019 were used to assess the available data for the whole year in detail.

Appendix D contains the results of the investigation. All refineries are categorised under the control of effluent limits. 5 of 20 refineries use "Current BAT Technologies" for wastewater treatment, 12 of 20 use "Biological Treatment" techniques, and 3 of them use "other than Biological Treatment techniques". All refineries discharge their effluents into the surface water, which are categorised with having flow, such as channels, bayou, rivers. 19 of 20 recipients contain the Endangered Species Act (ESA)-listed aquatic species – organisms, which live in the water and are characterised under the protection as vanishing. Half of those water bodies are used for different purposes, such as recreational use (9 of 20) and aquatic life use (11 of 20). 12 of 20 of those water bodies are listed for impairments by the EPA according to the Clean Water Act (USEPA 2015). It means that water quality has been already deteriorated by natural or anthropogenic factors. If the water body is already polluted, non-strict requirements can be applied for the belonged sources of the pollution. The substances, which cause the reason for impairment, include mostly organic matters, e.g. polychlorinated biphenyls (PCBs), pesticides, dioxins; the "total toxics", including mercury; pathogens; nutrients; and oil and grease. These substances occur in water through anthropogenic invasion.

The next step was to look at the concentrations of substances, using the Pollutant Loading and Effluent Charts tools of DMR. These tools present data, which have been collected from regular monitoring. Appendix E shows the extracted data from the Pollutant Loading Report of USEPA about monitoring status for the Top-20 Refineries in 2019. There is a twofold opportunity to look at the existing data. Firstly, the report is formed for the whole year. According to the NPDES, the refineries get a license to discharge a certain amount of pollutants based on their designed flow. No one refinery have shown exceeding the permissible loading into the aquatic system per year. Secondly, the monitoring system works constantly, and if the violation is identified, the system indicates it. In this case, it is interesting to note that Garyville Refinery, BP Whiting Refinery, Corpus Christi East Refinery and Wood River Refinery perform the monitoring for not only the pollutants of interest but they have extended the list of contaminants significantly. The updated list includes, for example, derivatives of phenolic compounds, toxic metals, per- and polyfluoroalkyl substances, etc. Those substances match with the substances, which caused impairments for local water bodies. Simultaneously, those refineries provide advanced wastewater treatment systems, including the usage of BAT Technologies. The exceedance of permissible limits, at least once per year, have been identified in 5 of 20 refineries. The amount of total suspended solids (2 refineries), oil and grease (2 refineries), sulphide (2 refineries), total organic carbon (2 refineries), BOD and ammonia has been exceeded (Appendix F). For example, The Philadelphia Refinery discharged 0.12 t sulphides more than has been planned in October 2019. The Deer Park Refinery loaded 0.95 and 4.69 t of oil and grease and total organic carbon, more than has been planned in October and November 2019. The Valero - Corpus Christi East Refinery sent 1.9 t more ammonia into the drainage ditch in November 2019.

3.2. The EU observation

The EU also aimed to solve the potential problems with the gaps in legislation. The shifting to the control of hazardous pollutants started in the 1970s, with the first implementation of the BAT in the 1990s (CONCAWE, 2012). The recent understanding of the fact that water resources have limited capacity, despite a general improvement of water quality, has driven the European Commission to revise constantly the crucial law documents, such as Directives (e.g. the Urban Waste Water Treatment Directive, the Drinking Water Directive, the Water Framework Directive (WFD)), seriously (Werner and Collins 2012). The milestone in the European environmental legislation: The Water Framework Directive, aimed to achieve "good status for surface and groundwater", which means to avoid the deterioration of the quality and quantity of water bodies and related ecosystems (EU 2000). While the implementation of the Directive has safeguarded the water resources, there are still opportunities to improve the system by dealing with existent gaps and disadvantages of the current version of the legislation (Tsani et al., 2020). Those opportunities include, for example, improvement of the monitoring systems, more complex assessment of the status of water bodies, support of solution-oriented management, etc. (Brack et al., 2017).

The EU also promotes a preventive approach for industrial emissions to reduce and eliminate any pollution. Directive on industrial emission (EU 2010) requires the following key steps for implementation to achieve the goal: (i) the integrated approach states avoiding the transfer of pollutants from one environmental medium to another; (ii) the responsibility should be assigned to any operator who generates emissions; (iii) holding permission for the emissions means that the set of best available technologies (BAT) appropriate techniques must be applied to protect the environment. This approach ensures that the quality of the emissions is not allowed to elevate critical concentrations, dangerous for the people and the environment.

The petrochemical industry in Europe is the main water-using industry within the manufacturing sector (Willet et al., 2019). Environmental issues caused by the oil refinery sector in Europe are managed by Concawe (an abbreviation of "CONservation of Clean Air and Water in Europe") – the organisation, which combines most oil companies operating in Europe. Their mission is to act in line with the concerns over environmental issues through the conductance of research programs to support cost-effective and safe decisions for the sector. Instead of the focus on the allowable concentrations of separated chemicals, the EU practices Whole Effluent Assessment (WEA) to test the response of local ecosystems to the mix of the discharged contaminants coupled with the operational monitoring of the status of the water bodies (CONCAWE 2012). The WEA approach is a tool, which aims to support the WFD in achieving the global aim of "good ecological status" for all European waters; and also to support in identification of BAT for the refinery industry under the Integrated Pollution Prevention & Control Directive (IPPC) for controlling pollution. The strategy of the assessment is based on the historical background, where the characteristics of receiving waters and effluents are already known for decades. Particular attention is paid to WET tests with the focus on the persistence, bioaccumulation or toxicity (PBT) properties of effluents or effluent constituents. The tests are carried out on living species, such as microorganisms, invertebrates and fish, to assess acute and chronic toxicity (CONCAWE 2004a). However, only 28 of 64 refineries reported their use of WEA with the most common method of short-term toxicity assessment, instead of the assessment of persistence and bioaccumulation (CONCAWE 2012). The Concawe perform both types of assessment of the influence of refinery effluents: they regularly carry out the surveys of effluent quality and water use at the refineries and, simultaneously, they analyse the application of the WEA by the refineries and produce their recommendations based on the results of the investigations.

The most recent report from the Concawe has been dated June 2020 (CONCAWE 2020a). 98 refineries have been called to share their statistics about water use issues, including the information of water consumption, discharge and related water quality data. 72 refineries provided the whole report, and results have been compared with the previous reports. The main appropriate outcomes from the report for this study are an assessment of the effluent discharge volume and the refinery effluent quality, coupled with the related trends. Most refineries clean their wastewater by themselves, and only a few of them (8.8%) send the wastewater to centralised urban treatment systems. More than half of the wastewater volume (51%) has been exposed to a three-stage wastewater treatment plant. 17% of wastewater has been treated by limited treatment techniques, such as physical and/or chemical only. That type of wastewater mostly belongs to lightly contaminated (e.g. rainwater water runoff).

The content of pollutants in the effluents from refineries in Europe shows a stable decrease since the 1970s (CONCAWE 2004b). The studies showed that there was significant damage to aquatic ecosystems by toxic substances, such as ammonia, sulfides, phenols and PAHs (Wake 2005). After the implementation of strict requirements and the stop of disposal of polluted effluents, there was hope for recovery.

Throughout the control of wastewater quality, the main focus is on hydrocarbons and related derivatives. Appendix G shows a summary of the reported values of the monitored contaminants. A detailed explanation of how much TPH/OiW, BTEX, phenols and PAHs have been discharged annually in different variations is presented. The amount of total TPH in effluents decreased from 44,000 t/y to 257 t/y during the period between 1969 and 2016. The reported mean annual concentration of TPH varied between 0.5 mg/L and 16 mg/L among the refineries, with an average concentration of 1.4 mg/L for all refineries. The same trend sounded for the phenol index with the descend from 179 t/y (0.41 g/t throughput in relative discharge) in the year 1993 to 29.6 t/y (0.058 g/t throughput in relative discharge) in 2016. However, there is a light increase comparatively with 2013. Also, the average annual concentration of phenols ranged between 0 and 0.62 mg/L among different enterprises, with an average concentration of 0.08 mg/L (Fig. 6). The analysis of the presence of PAHs and BTEX in wastewater has been started relatively recently, and the data only for 2010–2016 have been presented in the report. The effect of loading of these chemicals is unclear because the cumulative sum has shown safe concentrations, while the concentrations of the separated hydrocarbons, such as anthracene and fluoranthene, exceeded the recommended values (CONCAWE 2018). The concentrations are relatively the same for the reports 2013 and 2016. The content of total nitrogen and phosphorus, as the potential sources of hazard for living microorganisms, has shown reasonable values. Fig. 6 shows the variations of concentrations of mentioned chemicals in the discharges at EU refineries. Most of the reported sites (around 70%) show the values below mean concentrations, while around 5–10% significantly higher than average.

3.3. Kazakhstan observation

The water sector in Kazakhstan faces severe problems. Climate change would affect the quality of water resources, coupled with the decline of their quantity (Salnikov et al., 2015). According to Karatayev et al. (2017), poor water infrastructure and water pollution are the main current weakness and challenges, while water-saving potential in Kazakhstan is ranked as one of the major opportunities in the water sector. Even when it seems that the representatives of the government are satisfied by the water legislation, the nongovernmental organisations, together with academia, define the problems in the water management sector. For example, the limited access to existing data for researchers, despite the ratified Aarhus Convention.

Multiple barriers, such as the perception of the industry of pricing and technological changes, exist in the oil refinery sector in Kazakhstan. Currently, the price of water is very low for the industry, as well as the penalties for the violation of the current version of the law. Kazakhstan deals with the implementation of suitable legislation. The government of Kazakhstan applies efforts to improve the situation through policy strengthening. A new ecological code has been announced for adoption. The law claims the implementation of BAT, increased penalties and investment of industry for environment protection (PrimeMinister 2019). The implementation of the law aims the transition to sustainable development and a "green economy", with a focus not only on resource efficiency and waste prevention but on human well-being and ecosystem resilience as well (EEA 2015).

JSC NC "KazMunayGas" (KMG) is the national company in Kazakhstan, which operates all three refineries on the territory of Kazakhstan. The recent sustainability report claims to achieve and lead the initiatives of sustainable development, including the goals related to water-saving and efficiency (JSCNC"KazMunayGas", 2020). The company confirms its commitment to efforts to deal with the efficient use of water and taking responsibility to reduce and minimise environmental impact. The report has listed the following issues as a top prior-

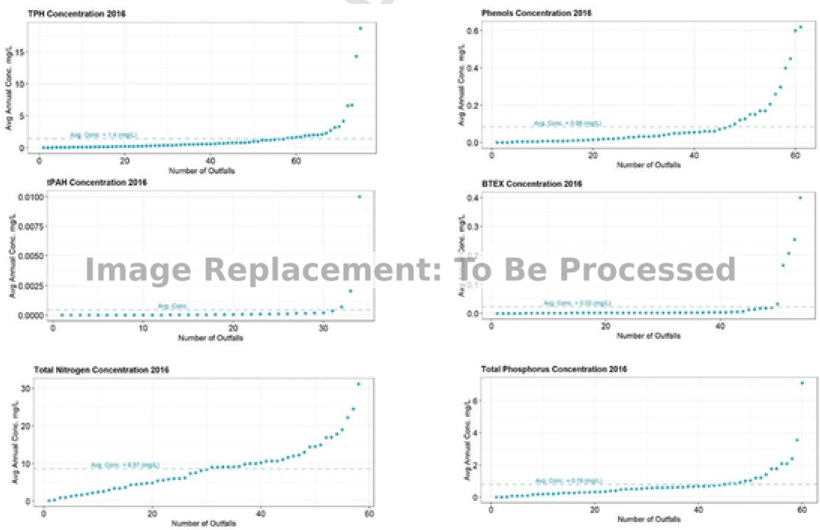

Fig. 6. The amount of key pollutants in the discharges from the refineries in the EU (CONCAWE 2020a).

ity: liquidation of historical contamination, reduction in pollutant emissions and an increase in volume or recycled and reused water.

The procedure of giving permission for emissions into the environment in Kazakhstan is regulated by the procedure of Environmental Impact Assessment (EIA). This assessment considers the type of industry, the conditions of the effluents and recipients. The maximum permissible discharges (MPDs) are calculated based on the above characteristics under the methodology from an Order of Ministry of Environmental Protection of the Republic of Kazakhstan (2012). The MPDs are calculated for any recipient separately by the following formula:

$$C_{MPD} = C_0 + \left(C_{TLV} - C_0\right) \times k \tag{1}$$

Where C_{MPD} is a calculated and established concentrations of the pollutants in wastewater; C_0 is a background concentration of the pollutant in the recipient; C_{TLV} is a threshold limit value, which is established by law about sanitary and epidemiological requirements for water sources; and k is a coefficient, which characterises total assimilating, evaporating, filtering capacity of the recipient. Therefore, if the wastewater recipient is a closed type water body, which is not used for any purposes, such as a source of drinking, irrigation, recreation, or domestic water; the MPDs are equal to the actual discharge of pollutants after treatment facilities, or

$$C_{MPD} = C_0 \tag{2}$$

The historical background of water use in the oil refinery industry and related issues was described by Radelyuk et al. (2019). The loopholes in legislation let the refineries use already polluted storage sites as the recipients of effluents. The reason why the storage sites have been polluted is that refinery, and other industries sent their improperly treated or untreated wastewater into the recipients during the soviet and post-soviet era. The concentrations of the pollutants in discharges have been established based on the background concentrations of the chemicals in the recipients (Table 3). Not strict requirements have been applied for the quality of the effluent. Even those insufficient requirements have been violated by the industry, which has been discovered when unexpected commissions take place (KapitalKZ 2019). While the formal criteria are followed by the enterprises, the hazard for the environment and health of people still exists. A recent study (Radelyuk et al., 2020) shows that there is a direct impact on groundwater surrounding one of the recipients (Appendix H), where the average exceedance for total petroleum hydrocarbons was four times on the distance 1 km from the source of contamination. The direct discharge without any treatment for the first three years of the refinery work caused the source of contamination in the soviet period. The study shows that natural processes, coupled with anthropogenic deteriorate groundwater quality. The recipient pond is considered as the receiver for a higher amount of wastewater in future due to industrialisation of the region, whereas the quality of them cannot be assured safe. The recent investigations by the authors showed that a distance of contamination plume of petroleum hydrocarbons could spread out on a distance of 2–6 km depending on the initial concentrations until the concentration reaches the safe limit. It could affect the water quality using for irrigation (Radelyuk et al., 2021). Due to the drawbacks of the Kazakhstani management system, such as lack of data, lack of transparency, poor engagement of stakeholders into the collaborative work with academia, etc., there is still difficult to evaluate real conditions of the potential hazards. KMG plans to maintain the renovated equipment with advanced treatment techniques coupled with the program of recultivation of the recipient of Atyrau Refinery. However, the whole process would take place until 2023. The situation with the PKOP refinery, which is a part of the KMG group, seems better, as they use the long buffer channel with waterproofing bottom to send their effluents, firstly, to the evaporation pond, and after that to the local water body.

Table 3
Maximally permitted concentrations of different parameters in the effluents of three Kazakhstan oil refineries (Radelyuk et al., 2019).

Parameter	Units	Refinery X	Refinery Y	Refinery Z
Ammonia ($NH_4^{\ +}$)	mg/L	55.18	8.0	4.53
Total petroleum hydrocarbons (TPH)	mg/L	3.02	8.0	2.03
Biochemical consumption of Oxygen (BOD)	mgO_2/L	17.82	16.6	11.6
Nitrates ($NO_3^{\ -}$)	mg/L	19.2	7.8	8.96
Nitrites ($NO_2^{\ -}$)	mg/L	7.7	0.5	–
Sulphates ($SO_4^{\ 2-}$)	mg/L	643.05	500.0	471.1
Phenol's index	mg/L	0.25	0.05	0.182
Chlorides (Cl^-)	mg/L	169.8	350.0	678.8
Suspended solids	mg/L	20.98	25.75	6.05
Surfactants	mg/L	0.52	2.80	1.27
Phosphates ($PO_4^{\ 3-}$)	mg/L	1.05	2.0	6.89
Total Dissolved Solids (TDS)	mg/L	–	6000	–

"-"- not controlled.

4. Discussion

This section analyses the results by, firstly, comparison between policies in different countries; secondly, comparison of differences in treatment and discharge techniques; and, thirdly, comparison of ways and progress towards the SWU in the sector, weaknesses and strengths on the local level, and possible ways to overcome obstacles towards the SWU. Table 4 summarises the results of the performed observations coupled with sound examples from a literature review.

This study identified that effective policy is an efficient *response* to achieve sustainable water use in the oil refinery sector in Kazakhstan. The best option to assure safe water is efficient water and wastewater management of water users, instead of post-factum attempts to clean already polluted sources (Fawell 2015). The effective management of industrial water use includes appropriate technology standards coupled with sufficient operational monitoring, which aims to prevent contamination. Thus, the *response* includes implementation of 1) the concept of circular economy (CE) (via 1a) water reuse and 1b) Best Available Techniques (BAT)); 2) Improved methodology for Environmental Impact Assessment (EIA), aiming to toughen the requirements for wastewater quality and characteristics of their recipients; and 3) Improved system of environmental monitoring.

4.1. Circular economy

Circular economy (CE) is a concept, which has relatively begun to be promoted in the western world and widely but slowly spreading through the other nations (Schroeder et al., 2019). The core of the concept is the transition from "linear model" of "linear economy" ("take-make-consume and dispose of") when the resources are transformed into the final product, which is consumed and subsequently wasted; to circular form, or even 10 Rs - "reduction and reuse, recycling and composting, and energy recovery" approach (Fan et al., 2020) when the waste, generated during the manufacturing process, are subject to 10Rs, and all resources are re-used again as much as possible (Smol et al., 2020).

The industry is the place where the concepts of the SWU and CE meet and interconnect with each other (Fan et al., 2019). The "win-win-win" (economic-social-environmental) potential of the circular economy contributes to all three dimensions of SD (Korhonen et al., 2018). The application of both is important on any level, from small-sized companies to international consortiums (Lewandowski 2016) through shared research, demonstration projects, and policy cooperation (Baas and Baas 2005). Schroeder et al. (2019) have identified relationships between CE and SDGs and have highlighted that one of the strongest relationships and synergies are between CE practices and water-related goals, among others. Concerns about environmental pol-

Table 4
Main outcomes from the performed observations with sound examples from an extended literature review.

Principle	USA	EU	Kazakhstan	Determining publications	Application of the principle	Improvement of the principle and usage as a tool for transition to the SWU
Circular Economy	•"In plant" and "End-of-pipe" approaches	•Priority of the strategies and promotion on the federal level	•Formal promotion and willingness to improve the situation (PrimeMinister 2019; JSCNC"KazMunayGas", 2020)	*Water rationalization*: Description (Wang and Smith 1994);	Application of Water Source Diagram (WSD) method (de Souza et al., 2009);	Constant water auditing to improve water conservation (Barrington et al., 2013);
	•BAT (USEPA 2015)	•BAT (EU 2014, 2020)		Review of conceptual and mathematical models (Bagajewicz 2000);	Proposed synthesis of water allocation and mass exchange network (Karthick et al., 2010);	Aiming zero liquid discharge and respective improvements of existing opyimization techniques (Maheshwari et al., 2019);
				Focus on multicomponent content of wastewater reused (Savelski and Bagajewicz 2003)	Proposal for use in Iranian refineries, considering different conditions of reused wastewater (Mohammadnejad et al. 2011, 2012);	Reuse of municipal wastewater at refineries (Johnson 2019)
				Environmental footprint: (Čuček et al., 2012)	Prospects for water rationalization practices in Brazilian refineries (Pombo et al., 2013)	
Environmental Impact Assessment	•NPDES with Assessment of the recipients	•Whole effluents assessment (CONCAWE 2012)	•Legislative loopholes (Kazakhstan 2012)	Assessment of pioneering toxicity testing of the effluents (Chapman et al., 1994);	Characterization of oil refinery effluents, specifically PAHs, PCBs, metals, and TOC in sediments and biota in the receiving river in the US (Hall and Burton 2005);	Discussion of the efficiency of conventional toxicity tests in the context of the new European water-related directives (Comber et al., 2015);
	•Whole effluents assessment (USEPA 2020)			Investigation of impact of efflunts on aquatic species (Bleckmann et al., 1995)	Assessment of nuclear abnormalities in fishes affected by oil refinery effluents (Cavas and Ergene-Gozukara 2005);	Investigation of behaviors of naphthenic acids (Wang et al., 2015) and their derivatives (Wang et al., 2019);
					Examining the main and interaction effects among components in the effluents (Parvez et al., 2008); Comparison the combination of persistency, bioaccumulation, and toxicity tests to an approach using only toxicity tests (Leonards et al., 2011);	Discussion of efficiency of toxicity testing on certain parameters (Daflon et al., 2017)
					Genotoxicity tests of effect of refinery effluents in India *in vitro* (Gupta et al., 2015) and *in vivo* in plant, animal and bacterial systems (Gupta and Ahmad 2012)	
Operational monitoring	•USEPA permanent monitoring and control	•Directives on industrial emission and integrated pollution prevention and control	•Limited indicators for monitoring	Identification of contaminants and their levels in the effluents and the recipients (Burks 1982; Snider and Manning 1982; Wake 2005)	Warning to monitor quality of the effluents and the reciving bodies after investigation of affected rivers (Vallieres et al., 2007; Hoshina et al., 2008), groundwater (Ripper and Fruchtenicht 1989; Hayat et al., 2002), sediments and living species in marine environment (Pettersen et al., 1997; Ruiz-Fernandez et al., 2016; Hara and Marin-Morales 2017)	Recommendations to revise parameters for monitoring after accidental discharge (Bandyopadhyay 2011);

Principle	USA	EU	Kazakhstan	Determining publications	Application of the principle	Improvement of the principle and usage as a tool for transition to the SWU
	•Extended list of contaminants (USEPA 2019)	•CONCAWE control and guidance (CONCAWE 2018)	•Lacking permanent control (Radelyuk et al., 2019)			Development of remediation practices for monitored pollutants (Janbandhu and Fulekar 2011)

lution and resource conservation are met in the concept of CE the same as for sustainable water use. According to (Bocken et al., 2014), technological aspects are the key element in achieving SD and CE. The importance of wastewater reuse has been highly emphasised in the context of CE. Achieving sufficient water quality is impossible without appropriate treatment approaches, which is the core of the BAT approach (Voulvoulis 2018).

First schemes of water use rationalization were proposed in publications from the early 2000s (e.g., Bagajewicz 2000). This concept received considerable attention and began to be improved and incorporated into the water management systems in oil refineries worldwide (e.g., Pombo et al., 2013). Currently, a combination of water and environmental awareness addresses the aims of the SWU. For example, water auditing can be used to identify both the current weaknesses of site water management and the potential for technical and behavioural improvements, including through aligning corporate strategy with water management goals (e.g., Maheshwari et al., 2019).

In comparison with developed countries, refineries in Kazakhstan do not aim to re-use water. Achieving sufficient re-use water quality is impossible without appropriate treatment techniques, which is the core of the BAT approach. The principle of BAT is to find the most efficient and cheapest way to meet the requirements for safe or re-used water. While the industrial processes and content of generated WW are the same for refineries in the USA/EU and Kazakhstan, the significant difference between developed countries and Kazakhstan is the usage of the "in-plant control" principle and BAT. The basic biological treatment method (activated sludge), which is used by refineries in Kazakhstan, cannot efficiently treat for two reasons: firstly, the petroleum hydrocarbons are heavily degradable, and secondly, salinity and toxicity of wastewater inhibit the efficiency of biomass. It means that there are requirements not only for finally treated effluents but for the quality of generated WW after each technological unit either. It leads to additional preliminary treatment, which reduces the burden on the final (or "end-of-pipe") treatment system and enhances the efficiency of it. As the generated wastewater consists mainly of salty unprocessed heavy oil-water emulsions, and even after primary mechanical treatment, there is a challenge to remove hydrocarbons from wastewater (Bruno et al., 2020). The basic biological treatment method (activated sludge), which is used by refineries in Kazakhstan, cannot efficiently treat for two reasons: firstly, the petroleum hydrocarbons are heavily degradable, and secondly, salinity and toxicity of wastewater inhibit the efficiency of biomass. Refineries in other countries solve this issue by using advanced techniques on each step of treatment: pre-, secondary, and post- (or polishing) treatment.

The implementation of BAT became one of the leading factors towards the transition to a circular economy (Pinasseau et al., 2018). However, even developed countries have not met the requirements for their technical capacity to meet the criteria of CE practices yet (IWA 2016). It should also be all the time be kept in mind that a circular economy is a tool, but the ultimate target is to minimise environmental footprints (Čuček et al., 2012). This becomes even more evident when the world is going through the COVID-19 pandemic (Klemeš et al., 2020a) and with the rising challenges providing an opportunity for a substantial innovation step (Klemeš et al., 2020b).

4.2. Environmental impact assessment

While there is a unified formal aim for all – to sustain the safe water system and eliminate the impact of wastes, there is no universal way to achieve and evaluate this goal. There are two general approaches – 1) to achieve safe concentrations for the ecosystem preliminary. And here is a potential bias depending on the decision-makers – how to calculate "safe concentrations" for a certain site. 2) to set the common rules for every player on the market.

There are different approaches in Kazakhstan and the EU/USA to make the process of implementation of the EIA efficient and transparent. Related decisions are taken by respective policy standards in both cases. However, both the USA and EU base their decisions and develop their strategies on the scientific approach (Zijp et al., 2016). The design of policy implementation for EIA in the EU has been based on the relevant scientific investigation through the possibility of integrating the respective technological development, well designed, clearly explained and regularly evaluated (Voulvoulis et al., 2017).

Toxicity testing (e.g., Chapman et al., 1994; Bleckmann et al., 1995) is historically acknowledged as the most efficient way to evaluate the safety of the effluents. There is a common practice when the results of investigations become publicly available and transparent. As examples can serve the detailed assessment of the effluents from refineries on aquatic ecosystems with a specific focus on PAHs, PCBs, metals, etc. (e.g., Gupta and Ahmad 2012). The process of effluents assessment continuously updated based on already existed knowledge, for example, assessment of new potentially bioaccumulative substances (PBS) (e.g., Comber et al., 2015), derivatives of naphthenic acids (e.g., Wang et al., 2019), or application of the toxicity tests to evaluate the efficiency of new treatment techniques specifically chosen for certain parameters (Daflon et al., 2017).

The current scheme of Environmental Impact Assessment in Kazakhstan is weakened by the respective legislative loophole. A Kazakhstani methodology (Equations (1) and (2)) is used to assess the environmental status of final effluent-water. There is a potential bias that maximum admissible concentrations have been set not in accordance with principles of sustainability and have used gaps in the legislation, which lets to discharge inappropriately treated wastewater. The whole methodology might be affected and represent the wrong score from the first step, which leads to environmental pollution. In contrast, the unconditional requirements for effluents safety assessment, such as a detailed investigation of effluents characteristics using, e.g., Parameter-Specific Approach, Whole Effluent Toxicity (WET) Approach, or Bioassessment Approach toxicity tests, have shown the high efficiency in the developed countries. The current conditions of discharges in the USA and the EU have shown a positive trend, as requirements for them are established based on reliable techniques of the EIA.

Also, that is a very unusual practice when the wastewater releases into the ponds with the affection on groundwater, like in the Kazakhstani case. And even if it is formally eligible, the unexpected commissions and complaints from the local habitats on the perception of groundwater quality shed light on the disadvantage of those pitfalls. In contrast, the EU directly forbids the transfer of pollutants from one environmental media to another. This ban has contributed to environmental improvements and promote both the governments and the industries to follow the SWU.

However, there is not full confidence in the "safety" of treated wastewater for two reasons. Firstly, the fate of hydrocarbons has not yet fully explored. For example, the recent study of PAHs degradation shows that the products of degradation are hazardous (CONCAWE 2020b). Secondly, several refineries still show high concentrations of contaminants, permanently or accidently, which requires additional investigations.

4.3. Operational monitoring

Overview of the improvements resulted in the identification of separated compounds supported with the future establishing criteria for effluents assessment since the early 1980s (e.g., Snider and Manning 1982). Identification of new substances in the effluents supported in the identification of hazardous substances, fractions and establishing their permissible levels. Wake (2005) published a substantial review of trends identified positive trends in Europe, concerned about already polluted sites. The potential fate for the environment and ecosystems from real case studies has been studied and presented for affected river and fish there (e.g., Hoshina et al., 2008), on groundwater (e.g., Ripper and Fruchtenicht 1989), on sediments and living species in a marine environment (e.g., Hara and Marin-Morales 2017). All these findings highlighted the necessity for adequate operational monitoring for both effluents and receiving water bodies. Operational monitoring is important as it helps to define the parameters needed to be revised as a result of the activities of the oil refineries (Bandyopadhyay 2011); or to develop respective remediation practices for monitored pollutants (Janbandhu and Fulekar 2011).

While the developed countries identified certain indicators, such as polycyclic aromatic hydrocarbons (PAH), naphthenic acids, PFAS, or benzene, toluene, ethylbenzene, xylene (BTEX), for better estimation of the toxic effect of their existence in wastewater; Kazakhstani oil refineries monitor only the sum of TPH, without detailed investigation of the resulted effect on the environment. Still, mentioned petroleum compounds are not degradable, which might cause risks even at low concentrations. Continuous update of the list of substances for operational control during the wastewater treatment and environmental monitoring in developed countries ensures environmental safety and follows the sustainable development principles positively affecting the monitoring system. E.g., US EPA carries out permanent control of the quality of wastewater and recipients to detect any accidental or other exceedance of permissible values for contaminants. In the EU, any operator of pollution monitors their emissions under the directives on industrial emission and integrated pollution prevention and control.

5. Conclusions

Delivery of SDGs requires a healthy and productive environment. The situation when the industry causes risks for the environment and public safety violates the principles of equitability and bearability of the SWU in Kazakhstan. This work was to compare the strategies of the implementation of the SWU system in the oil refinery industry between developed and developing countries. While the oil refinery industry discharges the effluents into the environment worldwide, the examples of chosen countries show that there are different approaches to ensure or not their safety. In order to achieve the SWU, the system of industrial water and wastewater management should rely on legislative and normative standards. The defined criteria should be implemented to ensure equitable access of different water users and viable mechanisms to achieve water safety are 1) implementation of the concept of Circular Economy (CE), via the implementation of Best Available Techniques (BAT) and water reuse, 2) an adequate and fair system of Environmental Impact Assessment, and 3) an adequate scheme of operational monitoring for wastewater quality. The considered principles should follow the requirement to control the amount of contamination inside the technological processes before final discharge.

It was found that the current "*status quo*" in Kazakhstan includes formal approval for polluting activities by the industry. The system is seriously weakened not only by gaps in legislation, rather by the not sufficient development of appropriate environmental tools (such as operational monitoring and preliminary and permanent environmental assessment). The performed investigations showed that decision-makers in Kazakhstan do not follow scientifically approved techniques and mechanisms to prevent pollution, which guarantees a good-status of receiving water bodies, comparatively with developed countries. The current trend in well-developed countries is a transition towards a "closed-loop" system. Comparatively, refineries in countries like Kazakhstan still need to implement the aim to re-use water, which does not reflect a risk of water scarcity in the region. Also, the current wastewater treatment scheme does not use efficient advanced techniques on each step, including pre-, secondary, and post- (or polishing) treatment. Thus, it is highly emphasised to improve the wastewater treatment systems via the implementation of the BAT.

Multiple barriers, such as the perception of the industry of pricing and technological changes, slow down the process of implementing the suggested *responses* in the oil refineries in Kazakhstan. The primary action should be the changing of the policy, which has not been updated for years.

CRediT authorship contribution statement

Ivan Radelyuk: Conceptualization, Methodology, Investigation, Formal analysis, Writing – original draft, Writing – review & editing. **Kamshat Tussupova:** Conceptualization, Methodology, Supervision, Formal analysis, Writing – review & editing. **Jiří Jaromír Klemeš:** Conceptualization, Supervision, Writing – original draft, Writing – review & editing. **Kenneth M. Persson:** Conceptualization, Supervision, Writing – review & editing.

Declaration of competing interest

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Appendix A. Supplementary data

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Appendix A. SDGs related to industry.

SDG	Targets	Indicators
SDG3 "Good Health and Well-Being"	3.9 By 2030, substantially reduce the number of deaths and illnesses from hazardous chemicals and air, water and soil pollution and contamination	3.9.2 Mortality rate attributed to unsafe water, unsafe sanitation and lack of hygiene (exposure to unsafe Water, Sanitation and Hygiene for All (WASH) services) 3.9.3 Mortality rate attributed to unintentional poisoning.
SDG6 "Clean Water and Sanitation"	6.3 By 2030, improve water quality by reducing pollution, eliminating dumping and minimizing release of hazardous chemicals and materials, halving the proportion of untreated wastewater and substantially increasing recycling and safe reuse globally	6.3.1 Proportion of wastewater safely treated 6.3.2 Proportion of bodies of water with good ambient water quality.
	6.4 By 2030, substantially increase water-use efficiency across all sectors and ensure sustainable withdrawals and supply of freshwater to address water scarcity and substantially reduce the number of people suffering from water scarcity	6.4.1 Change in water-use efficiency over time 6.4.2 Level of water stress: freshwater withdrawal as a proportion of available freshwater resources
	6.6 By 2020, protect and restore water-related ecosystems, including mountains, forests, wetlands, rivers, aquifers and lakes	6.6.1 Change in the extent of water-related ecosystems over time
SDG8 "Decent work and economic growth"	8.1 Sustain per capita economic growth in accordance with national circumstances and, in particular, at least 7 per cent gross domestic product growth per annum in the least developed countries	8.1.1 Annual growth rate of real GDP per capita
	8.2 Achieve higher levels of economic productivity through diversification, technological upgrading and innovation, including through a focus on high-value added and labour-intensive sectors	8.2.1 Annual growth rate of real GDP per employed person
	8.4 Improve progressively, through 2030, global resource efficiency in consumption and production and endeavour to decouple economic growth from environmental degradation, in accordance with the 10-year framework of programmes on sustainable consumption and production, with developed countries taking the lead	8.4.1 Material footprint, material footprint per capita, and material footprint per GDP 8.4.2 Domestic material consumption, domestic material consumption per capita, and domestic material consumption per GDP
SDG9 "Industry, Innovation and Infrastructure"	9.4 By 2030, upgrade infrastructure and retrofit industries to make them sustainable, with increased resource-use efficiency and greater adoption of clean and environmentally sound technologies and industrial processes, with all countries taking action in accordance with their respective capabilities.	9.4.1 CO2 emission per unit of value added.
	9.5 Enhance scientific research, upgrade the technological capabilities of industrial sectors in all countries, in particular developing countries, including, by 2030, encouraging innovation and substantially increasing the number of research and development workers per 1 million people and public and private research and development spending	9.5.1 Research and development expenditure as a proportion of GDP 9.5.2 Researchers (in full-time equivalent) per million inhabitants

SDG11 “Sustainable Cities and Communities”	11.6 By 2030, reduce the adverse per capita environmental impact of cities, including by paying special attention to air quality and municipal and other waste management.	11.6.2 Annual mean levels of fine particulate matter (e.g. PM2.5 and PM10) in cities (population weighted)
SDG12 “Responsible Consumption and Production”	12.2 By 2030, achieve the sustainable management and efficient use of natural resources.	12.2.1 Material footprint, material footprint per capita, and material footprint per GDP 12.2.2 Domestic material consumption, domestic material consumption per capita, and domestic material consumption per GDP
	12.5 By 2030, substantially reduce waste generation through prevention, reduction, recycling and reuse	12.5.1 National recycling rate, tons of material recycled
	12.6 Encourage companies, especially large and transnational companies, to adopt sustainable practices and to integrate sustainability information into their reporting cycle.	12.6.1 Number of companies publishing sustainability reports
SDG13 “Climate Action”	13.2 Integrate climate change measures into national policies, strategies and planning.	13.2.1 Number of countries that have communicated the establishment or operationalization of an integrated policy/strategy/plan which increases their ability to adapt to the adverse impacts of climate change, and foster climate resilience and low greenhouse gas emissions development in a manner that does not threaten food production (including a national adaptation plan, nationally determined contribution, national communication, biennial update report or other)
SDG14 “Life below Water”	14.1 By 2025, prevent and significantly reduce marine pollution of all kinds, in particular from land-based activities, including marine debris and nutrient pollution	14.1.1 Index of coastal eutrophication and floating plastic debris density
SDG17 “Partnership for the Goals”	17.14 Enhance policy coherence for sustainable development	17.14.1 Number of countries with mechanisms in place to enhance policy coherence of sustainable development

Appendix B. Mean concentrations and estimated loadings of contaminants in the directly discharged treated wastewater (USEPA 2019)

Pollutant	Average Pollutant Concentrations (mg/L*)	Estimated Loading (t/y**)
Ammonia as N	3.50	1,846.1
Arsenic	0.0179	9.4
BOD_5 (biochemical oxygen demand)	8.49	4,477.0
BTEX	0.000192	0.1
Cadmium	0	0
Chromium	0.00245	1.3
COD (chemical oxygen demand)	76.1	4,0142.9
Copper	0.00333	1.8

Cyanide	0.0122	6.4
Lead	0.000982	0.5
Mercury	0.0000860	0.04
Nickel	0.00547	2.9
Nitrate-Nitrite	No Data	No Data
Nitrogen, Total	16.9	8,890.4
Oil & Grease	2.16	1,138.5
PAH	No Data	No Data
Phenol	0.00894	4.7
Phosphorus	0.954	503.5
Selenium	0.0536	28.3
Sulfide	0.0296	15.6
TDS (total dissolved solids)	1440	762,035,2
TKN (total Kjeldahl nitrogen)	6.78	3,574.3
TOC (total organic carbon)	11.2	5,896.7
TSS (total suspended solids)	12.9	6,803.9
Uranium-238	No Data	No Data
Zinc	0.0261	13.8

Appendix C

Searching methodology:

1. Use the list of Refineries in the Appendix A and B from the Detailed Study of the Petroleum Refining Category – September 2019 Report, EPA, Washington D.C. (USEPA 2019);
2. Selection criteria: **Discharge status**: "Direct" or "Direct and Indirect"; **2018 EIA Refinery Atmospheric Crude Distillation Capacity (barrels per calendar day)**: Top-20 refineries;
3. Search an individual case for each refinery (https://echo.epa.gov/trends/loading-tool/water-pollution-search) by using **NDPES ID** for **Facility ID**;
4. Select **Reporting Year 2019** in the created **Pollutant Loading Report (DMR);**
5. Download all data for **Top Pollutants by Pounds** and for **Top Pollutants by Toxic-Weighted Pounds (TWPE);**
6. Observe the recipient characteristics from **Receiving Water Information** tab;
7. Follow the link to create **Detailed Facility Report;**
8. In the tab **Environmental conditions** observe characteristics of **Water body designated use.**

Appendix D. Characteristics of recipients of treated refinery wastewater

Refinery Name	Refinery capacity (barrels per calendar day)	NPDES ID(s)	Operating company	WWT Categories	Water Body Name	Exceptional use	Recreational use	Aquatic Life use	Shellfish use	Listed for Impairment	Cause(s) for Impairment	Facility pollutant(s) potentially contributing to impairment	Discharges to a county or watershed with ESA-listed aquatic species
Motiva - Port Arthur Refinery	603000	TX0005835	Motiva enterprises - Divested to Saudi Aramco	Biological Treatment	ALLIGATOR BAYOU (CANAL D), MAIN OUT	No	Yes	Yes	No	Yes	TOTAL TOXICS	Chromium; Chromium, Hexavalent; Cyanide	Yes
Marathon - Galveston Bay Refinery	571000	TX0003522	Marathon Petroleum Corporation	Current BAT Technology	TEXAS CITY SHIP CH;HURRICANE CANAL Dickinson Bayou	No	Yes	Yes	No	Yes	DIOXINS, POLYCHLORINATED BIPHENYLS (PCBS)	None found	Yes
Baytown Refinery	560500	TX0006271	ExxonMobil	Current BAT Technology (Chemical oxidation)	HOUSTON SHIP CHANNEL/SAN JACINTO RI Goose Creek-Frontal Galveston Bay	No	No	No	No	No			Yes
Garyville Refinery	556000	LA0045683	Marathon Petroleum Corporation	Current BAT Technology (Effluent settling pond)	Mississippi River Dutch Bayou-Mississippi Bayou	No	No	No	No	No			Yes
Baton Rouge Refinery	502500	LA0005584	ExxonMobil	Biological Treatment	Mississippi River Manchac Point	No	No	No	No	No			Yes
Citgo - Lake Charles Refinery	418000	LA0005941	Citgo Petroleum Corporation	Biological Treatment	Indian Marais Calcasieu River-Prien Lake	No	Yes	Yes	No	Yes	NUTRIENTS, ORGANIC ENRICHMENT/OXYGEN DEPLETION, PESTICIDES, POLYCHLORINATED BIPHENYLS (PCBS), TOXIC ORGANICS	Ammonia as N; BOD, 5-day, 20 deg. C; Benz[a]anthracene; Benzene; Benzo[a]pyrene; Nitrogen; Phosphorus	No
BP Whiting Refinery	413500	IN0000108	BP	Current BAT Technology	LAKE MICHIGAN Calumet River-Frontal Lake Michigan	No	Yes	Yes	No	Yes	CAUSE UNKNOWN, MERCURY, OIL AND GREASE, PATHOGENS, PESTICIDES, POLYCHLORINATED BIPHENYLS (PCBS), TOXIC ORGANICS	Benzo[a]pyrene; Mercury; Oil and grease	Yes
Beaumont Refinery	365644	TX0118737	ExxonMobil	Treatment Other than Biological Treatment (second oil/separation unit)	UNNAMED ARM OF THE NECHES RIVER TIDAL	No	No	No	No	No			Yes

Pascagoula Refinery	352000	MS0001481	Chevron Corporation	Biological Treatment	Bayou Casotte	No	No	No	No	No			Yes
Philadelphia Refinery	335000	PA0011533; PA0012629	Philadelphia Energy Solutions Refining and Marketing LLC	Biological Treatment	City of Philadelphia-Schuylkill River	No	No	No	No	No			Yes
Valero - Port Arthur Refinery	335000	TX0005991	Valero Energy Corporation	Biological Treatment	JCDD #7 MAIN OUTFALL CANAL Salt Bayou	No	Yes	Yes	No	Yes	TOTAL TOXICS	Chromium; Chromium, Hexavalent; Cyanide; Lead; Mercury	Yes
Flint Hills - Corpus Christi East Refinery	319000	TX0006599	Flint Hills Resources	Current BAT Technology	CITY OF CORPUS CHRISTI STORM WATER Tule Lake	No	No	No	No	No			Yes
Wood River Refinery	314000	IL0000205	Phillips 66	Biological Treatment	Mississippi River Burrough's Branch-Cahokia Creek	No	Yes	Yes	No	Yes	MERCURY, METALS (OTHER THAN MERCURY), PATHOGENS, POLYCHLORINATED BIPHENYLS (PCBS)	Arsenic; Barium; Cadmium; Chromium; Chromium, Hexavalent; Coliform, fecal general; Copper; Iron; Lead; Manganese; Mercury; Nickel; Selenium; Silver; Vanadium; Zinc	Yes
Pine Bend Refinery	310000	MN0000418	Flint Hills Resources	Biological Treatment	Spring Lake-Mississippi River	No	No	Yes	No	Yes	MERCURY, POLYCHLORINATED BIPHENYLS (PCBS), TOXIC ORGANICS, TURBIDITY	Mercury	Yes
Catlettsburg Refinery	277000	KY0000388; KY0070718	Marathon Petroleum Corporation	Biological Treatment	Chadwick Creek-Big Sandy River	No	Yes	Yes	No	Yes	METALS (OTHER THAN MERCURY), SEDIMENT	Chromium; Chromium, Hexavalent; Iron; Solids, total suspended; Zinc	Yes
Valero - Corpus Christi East Refinery	275000	TX0006904	Valero Energy Corporation	Treatment Other than Biological Treatment (only Oil/water Separation)	UNNAMED DRAINAGE DITCH Tule Lake	No	No	No	No	No			Yes
Deer Park Refinery	275000	TX0004871; TX0004863	Shell Oil Products US and Pemex	Biological Treatment	Patrick Bayou Vince Bayou-Buffalo Bayou	No	No	Yes	No	Yes	DIOXINS, MERCURY, PATHOGENS, PESTICIDES, POLYCHLORINATED BIPHENYLS (PCBS), TOTAL TOXICS	Chromium; Chromium, Hexavalent; Copper; Enterococci: group D, MF trans, M-E, EIA	Yes
Chevron - El Segundo Refinery	269000	CA0000337	Chevron Corporation	Biological Treatment	Pacific Ocean Manhattan Beach-Frontal Santa Monica Bay	No	Yes	No	No	Yes	PATHOGENS	Coliform, total MF, immed, m-endo med 35 C; Enterococci: group D, MF trans, M-E, EIA	Yes

LyondellBasell - Houston Refinery	263776	TX0003247	LyondellBasell	Treatment Other than Biological Treatment (only Oil/water Separation)	Vince Bayou-Buffalo Bayou	No	No	Yes	No	Yes	DIOXINS, PATHOGENS, PESTICIDES, POLYCHLORINATED BIPHENYLS (PCBS)	Indeno[1,2,3-cd]pyrene; Naphthalene	Yes
Phillips - Lake Charles Refinery	260000	LA0003026; LA0104469	Phillips 66	Biological Treatment	Bayou Verdine-Calcasieu River	No	Yes	Yes	No	Yes	ORGANIC ENRICHMENT/OXYGEN DEPLETION, PESTICIDES, POLYCHLORINATED BIPHENYLS (PCBS), TEMPERATURE, TOXIC ORGANICS	1,2-Dichloroethane; 2-Methylnaphthalene; Anthracene; BOD, 5-day, 20 deg. C; Benz[a]anthracene; Benzo[a]pyrene; Chemical oxygen demand (COD); Chrysene; Dibenz[a,h]anthracene; Fluoranthene; Phenanthrene; Phenol; Pyrene	No

Appendix E. Data from the Pollutant Loading Report of USEPA about monitoring status for Top-20 Refineries. DMR

Pollutant Name	CHEVRON EL SEGUNDO REFINERY Total Pounds (lbs/yr)	CHEVRON EL SEGUNDO REFINERY Max Allowable Load (lbs/yr)	FLINT HILLS RESOURCES PINE BEND Total Pounds (lbs/yr)	FLINT HILLS RESOURCES PINE BEND Max Allowable Load (lbs/yr)	CONOCOPHILLIPS CO, ROXANA WOOD RIVER REFINERY Total Pounds (lbs/yr)	CONOCOPHILLIPS CO, ROXANA WOOD RIVER REFINERY Max Allowable Load (lbs/yr)
Total Organic Carbon					19739.61489	371902.7639
Solids, total suspended	254018.65	780735	37831.185	494162.55	224860	1743240
Oil and grease			0	174647.025	152963.6685	683624.0133
BOD, 5-day, 20 C	92084.5	975645	24733.485	507039.75	187985	881840
Nitrogen, nitrate dissolved			71172.21447		371627.3484	
Ammonia as N	36964.05	532170	4918.029795	564987.15	11320	1186980
Phosphorus			10314.4339		13778.8	43800
Zinc	34.63908987				1168.936932	
Sulfide			0	3702.195	1083.9	11680
Total phenols	82.8444	69204	0	4024.125	455.51	12410
Copper	3.129885058				47.29802616	
Chromium, Hexavalent			30.8259	515.088	144.81	1095
Chromium	102.72	7624.3	0	6680.0475	175.75	13870
Chemical oxygen demand (COD)	1521051.8	6813090	886230.072	4861947.825	1801560	15199330
Chloroform	3.937154497					
Total Residual Chlorine	41.59784378				1114.75328	1732.256348
Chloride			2404126.662		2508584.753	
Sulfate			7711710.379		53717044	
Solids, total dissolved			25076897.52			
Selenium	161.9801593		2827.33873		3243.293222	
Manganese					23412.52295	
Arsenic	14.07528692				74.32546968	
Vanadium					564.1978835	
Mercury			0.032098218	0.08720062	0.20453	87.6
Nickel	14.54299732				2229.76409	
Iron					18209.74007	
Cyanide					1577.539001	4380
Boron					15067.79976	
Barium					6216.31201	
Sodium			3452859.702			
Bicarbonate ion- (as HCO3)			2632325.3			
Magnesium			559576.0337			
Potassium			178828.3695			
Total Kjeldahl Nitrogen			77339.32792			
Perfluorohexane Sulfonate			0.251319871			
Perfluorohexanoic acid			0.166840718			
Perfluorooctanesulfonamide			0.103494407			
Perfluorovaleric acid			0.090870666			
Perfluorobutane Sulfonate			0.067440724			
PFOA			0.036980768			
Tridecafluoroheptanoic acid			0.033081711			
Methyl tert-butyl ether	3.143408293					

Pollutant Name	PORT ARTHUR REFINERY Total Pounds (lbs/yr)	PORT ARTHUR REFINERY Max Allowable Load (lbs/yr)	PHILADELPHIA REFINERY Total Pounds (lbs/yr)	PHILADELPHIA REFINERY Max Allowable Load (lbs/yr)	CATLETTSBURG REFINERY Total Pounds (lbs/yr)	CATLETTSBURG REFINERY Max Allowable Load (lbs/yr)
Total Organic Carbon	1324860.686	6660269.108	3788.942844	23006.76633	48327.34878	2828463.277
Solids, total suspended	1916681.887		91473.47835	423765	762815.3733	1712215
Oil and grease	561175.6965	2231413.822	41055.5	163196.5661	92816.83693	1031384.538
BOD, 5-day, 20 C	404648	2546605	103322	792050	75092	2072835
Ammonia as N	8496.65	697150	6006.677529	229950	3924.44	736205
Zinc					1.255508586	
Sulfide	1454.23	11424.5	1804.66	5621	1347.96	10950
Total phenols	411.9771429	27343.71429	126.945	2628	233.505	7665
Copper	221.11	1149.75				
Chromium, Hexavalent	0	2591.5	0	255.5	100.198	751.9
Chromium	0	22739.5	0	3102.5	80.764	8760
Chemical oxygen demand (COD)	4608490	16458580	427716	3530645	637985	14134260
Benzene, ethylbenzene, toluene, xylene combination			0	1724.869012		
Lead	293.41	8030	0	1087.924374		
Benzene			0	1724.869012		
Hexachlorobenzene			1.196275679			
Phenol			0	8624.345058		
Naphthalene			0	19663.50673		
Total Residual Chlorine					0	78.75774925
Solids, total dissolved			21576995.46	55195665		
Fluoride			28226	236520		
Mercury	13.14	23.36				
Iron			3386.911569		13268.14349	
Polychlorinated biphenyls			0.002489435			
Cyanide	0	408.8				

Pollutant Name	PASCAGOULA REFINERY Total Pounds (lbs/yr)	PASCAGOULA REFINERY Max Allowable Load (lbs/yr)	BP AMOCO WHITING REFINERY Total Pounds (lbs/yr)	BP AMOCO WHITING REFINERY Max Allowable Load (lbs/yr)
Total Organic Carbon	748820.2971	3209374.966	374493.7313	991448.2348
Solids, total suspended	209278	1848725	92732.5	1330790
Oil and grease	33283.86605	2068216.414	55369.6525	1542792.934
BOD, 5-day, 20 C	229658	2111525	0	1518765
Nitrogen, nitrate dissolved			144930	
Ammonia as N	12885	73876	0	375950
Phosphorus			11612.25298	56240.6848
Sulfide	637.1	11315	693.4	8431.5
Total phenols	53.63	8760	0	7420.45
Copper	3.88	897.9		
Chromium, Hexavalent	0	908.85	0	733.65
Chromium	0	10220		
Chemical oxygen demand (COD)	1967803	15262110	1768864	11067895
Total Residual Chlorine			0	7300
Chloride			10236216	
Sulfate			6864810	
Solids, total dissolved			31870983	
Strontium			19979	
Fluoride			17841	
Selenium			4905.5	
Manganese			724.31	
Arsenic			136.55	
Vanadium			92.35	4500
Mercury			0.092858823	0.385329062
Chromium			0	8723.5
Nickel	39.68	2190		

Appendix E. DMR

	CITGO PETROLEUM CORP		GARYVILLE REFINERY		BATON ROUGE REFINERY	
Pollutant Name	Total Pounds (lbs/yr)	Max Allowable Load (lbs/yr	Total Pounds	Max Allowable Load (lbs/yr)	Total Pounds (lbs/yr)	Max Allowable Load (lbs/yr)
Total Organic Carbon	572165.4792	4340677.886	32364.1284	398350.583	128897.2699	673296.2324
Solids, total suspended	310355.3549	1267629.721	267722.18	1073488.379	676614	2171159.975
Oil and grease	1108.839596	561996.1903	120990.686	475745.1749	0	1014113.87
BOD, 5-day, 20 C	197796.0095	1995911.939	104627	1204865	217027.5	2596610
Nitrogen, nitrate dissolved	929558.8				222846.7	
Ammonia as N	45091	953380	19385	689120	5728.266667	1149020
Phosphorus	73538.5				25104.7	
Zinc					1023.723913	
Sulfide	546	7482.5	577	6095.5	2225.7	12702
Total phenols	336.2	13213	271.4	7774.5	942.4	17191.5
Copper					63.01043179	
Chromium, Hexavalent	0	1095	146	1022	0	2080.5
Chromium	0	11935.5	401.5	12775	0	24126.5
Chemical oxygen demand (COD)			1336760	8371275	4244803	17817475
2,4-Dinitrophenol			18.25	131.4		
Acrylonitrile			10.95	10.95		
Benzene, ethylbenzene, toluene, xylene combination	51.33927327	138.6049494	9.46778424	286.9954959	0	95.69437605
Lead	10.53397616	27.72098989	5.73990992	57.39909919	49.9108849	19.13887521
Benzene	5.655081937	27.72098989	3.40538778	64.69909919	0	19.13887521
Hexachlorobenzene			3.65	21.9		
Benzo[k]fluoranthene			3.65	3.65		
Acenaphthene			3.65	3.65		
Chrysene			3.65	3.65		
Carbon tetrachloride			3.65	14.6		
Pyrene			3.65	3.65		
Benzo(b)fluoranthene			3.65	3.65		
Phenol			3.65	3.65		
m-Dichlorobenzene			3.65	14.6		
Hexachloroethane			3.65	21.9		
Diethyl phthalate			3.65	3.65		
Benz[a]anthracene	0	278.13	3.65	3.65		
Anthracene			3.65	3.65		
Acenaphthylene			3.65	3.65		
p-Dichlorobenzene			3.65	14.6		
Di(2-ethylhexyl) phthalate			3.65	10.95		
Nitrobenzene			3.65	244.55		
Naphthalene			3.65	3.65		
Fluorene			3.65	3.65		
o-Dichlorobenzene			3.65	21.9		
Hexachlorobutadiene			3.65	14.6		
Dimethyl phthalate			3.65	3.65		
Dibutyl phthalate			3.65	3.65		
Benzo[a]pyrene	0	278.13	3.65	3.65		
2,4-Dimethylphenol			3.65	3.65		
Phenanthrene			3.65	3.65		
Fluoranthene			3.65	3.65		
1,2,4-Trichlorobenzene			3.65	21.9		
1,1,2-Trichloroethane			0	3.65		
1,3-Dichloropropene			0	21.9		
4,6-Dinitro-o-cresol			0	7.3		
1,1-Dichloroethane			0	3.65		
trans-1,2-Dichloroethylene			0	3.65		
1,2-Dichloropropane			0	21.9		
Chloromethane			0	10.95		
Trichloroethylene			0	3.65		
Methylene chloride			0	3.65		
Chloroethane			0	10.95		
Tetrachloroethylene			0	7.3		
1,1-Dichloroethylene			0	3.65		
1,1,1-Trichloroethane			0	3.65		
o-Nitrophenol			0	7.3		
Chlorobenzene			0	14.6		
Vinyl chloride			0	10.95		
Ethylbenzene			0	14.6		
1,2-Dichloroethane			0	18.25		
p-Nitrophenol			0	18.25		
Toluene			0	3.65		
Chloroform			0	10.95		
Total Residual Chlorine	59.58656613					

	BEAUMONT REFINERY		FLINT HILLS RESOURCES, LP - EAST PLANT		SHELL OIL COMPANY DEER PARK REFINERY		LYONDELLBASEL - HOUSTON REFINERY		Phillips -Lake Charles Refinery	
Pollutant Name	Total Pounds (lbs/yr)	Max Allowable Load (lbs/yr	Total Pounds (lbs/yr)	Max Allowable Load (lbs/yr)	Total Pounds (lbs/yr)	Max Allowable Load (lbs/yr)	Total Pounds (lbs/yr)	Max Allowable Load (lbs/yr)	Total Pounds (lbs/yr)	Max Allowable Load (lbs/yr)
Total Organic Carbon					603427.0361	3292611.414	144278.7112	995302.5916	71435.24247	480042.166
Solids, total suspended	473758.6026		0	106580	73093	722700	1382748.18	3930830.783	369456	1713326
Oil and grease	45874.64057	546500.9457	6472.612326	46556.43362	116813.3901	711816.7316	137140.0401	289542.5721	39618	1608950.149
BOD, 5-day, 20 C	166545.771	1020135.099			29611.7	514650	134127.3982	832434.8948	142507.1	3063236
Nitrogen, nitrate dissolved					87128.88646				231852.2	
Ammonia as N	20682.74615		0	53290	3592.3	182500			71213.3	1187894
Phosphorus					13506.33311				18592.3	
Zinc			6.798423587				5267.230444	9229.169486		
Sulfide	2025.119506		0	693.5	679.63	3650				
Total phenols	553.8700795	11334.83443	24.4	1606	170.004	52560				
Copper					637.5002186	1215.45				
Chromium, Hexavalent	0	1275.168873	0	88.695						
Chromium	0	12751.68873	0	985.5	53.382	48180				
Chemical oxygen demand (COD)	1212916.619	7651013.239	92169.19608	842386.1051			894524.312	6243469.115	1911078	22127474
Aluminum										
PAH							5026.558362			
Benzene	10.03847859	19127.5331								

	PORT ARTHUR OIL REFINERY		GALVESTON BAY REFINERY		EXXONMOBIL REFINING & SUPPLY BAYTOWN REFINERY, BAYTOWN, TX 77520	
Pollutant Name	Total Pounds (lbs/yr)	Max Allowable Load (lbs/yr)	Total Pounds (lbs/yr)	Max Allowable Load (lbs/yr)	Total Pounds (lbs/yr)	Max Allowable Load (lbs/yr)
Total Organic Carbon	1643609.23	5211083.317	131715.789	1764897.789	2448731.068	19033683.24
Solids, total suspended	569430	2176065.313	17216.20778	153358.3149	2007168	5408935
Oil and grease	298699.7877	6485394.27	134820.1576	446157.5806	894161.8683	13111317.61
BOD, 5-day, 20 C	207492	2288139.673	359592.194	4366130	571409	2849920
Nitrogen, nitrate dissolved					162067	
Ammonia as N	50890	754067.9972	40503.76504	2324320	102452	730000
Zinc			2826.946	95995	22205.49997	
Sulfide	502.4	12449.46209	0	589	7920	322806
Total phenols	126.6	17210.40825	0	744	766.32	77263.2
Copper					79.98893093	
Chromium, Hexavalent	0	1421.52154	479.7611587	80121.89353	0	3650
Chromium	18	47283.03498	0	877.3	0	19005
Chemical oxygen demand (COD)	4079397	15850456.97				
Aluminum			268.311724			

Appendix E. Data from the Pollutant Loading Report of USEPA about monitoring status for Top-20 Refineries. TWPE

	Phillips -Lake Charles Refinery		LYONDELLBASEL - HOUSTON REFINERY		SHELL OIL COMPANY DEER PARK REFINERY	
Pollutant Name	Total TWPE (lbs-eq/yr)	Max Allowable TWPE (lbs-eq/yr)	Total TWPE (lbs-eq/yr)	Max Allowable TWPE (lbs-eq/yr)	Total TWPE (lbs-eq/yr)	Max Allowable TWPE (lbs-eq/yr)
Sulfide	1083.6	44597.868				
Ammonia as N	79.046763	1318.56234				
Chromium	11.5381	910	7.336411677	729.6763183		
Chromium, Hexavalent	104.0196	534.3015	62.71333063	550.0796566		390.915
Zinc	510.6421367		210.6892178	369.1667794		
Copper	2005.136071					
Hexachlorobenzene						8459.92182
Benzo[a]pyrene	0	11536.6426				24248.994
Chrysene	1299.9392					
Benz[a]anthracene	0	3517.3809	0	21659.775		7057.1655
Benzo(b)fluoranthene						7385.994
Benzo[k]fluoranthene						7050.267
Anthracene						584.073
Fluoranthene						336.384
Fluorene						160.965
Hexachlorobutadiene						131.0715
Carbon tetrachloride						64.532
Di(2-ethylhexyl) phthalate						269.1875
Hexachloroethane						39.42
Pyrene	3.9384					23.652
p-Dichlorobenzene						10.9865
2,4-Dinitrophenol						6.030301297
Acenaphthene						6.8985
Benzene			22.67757161	244.3015452		11.607
Phenol	51.76570472					
1,2,4-Trichlorobenzene						14.235
o-Dichlorobenzene						8.03
Dibutyl phthalate						2.8105
Nitrobenzene						2.8105
m-Dichlorobenzene						3.2485
Naphthalene			0	180.9641076		2.2995
2,4-Dimethylphenol						1.785759795
Acenaphthylene						1.936421053
Dimethyl phthalate						0.649270588
Diethyl phthalate						0.5823867
Tetrachloroethylene						52.8885
1,1,2-Trichloroethane						6.57
p-Nitrophenol						3.674491921
Chlorobenzene						0.460564543
1,1-Dichloroethane	0.058354708	0.018248365				0.118106657
trans-1,2-Dichloroethylene						0.020145611
Trichloroethylene						2.19
Chloroethane						3.468668062
Vinyl chloride						239.294
Methylene chloride						0.421458864
Chloromethane						4.811990318
Chloroform						0.455167167
1,3-Dichloropropene						169.652
1,2-Dichloropropane						47.961
Toluene			7.309444044			1.520074182
1,1-Dichloroethylene						78.913
1,1,1-Trichloroethane						1.029232615
Ethylbenzene			0.358809345	35.78289847		0.474281
Total Residual Chlorine	0	89.61854265				
Mercury	230.4158706					
Nickel	26.58263381					21.535
Xylene			7.182455225			
o-Chlorophenol						16.2425
Phenanthrene	21.112					66.6855
1,2-Dichloroethane						7.1175
2,4-Dichlorophenol						36.792
2,6-Dinitrotoluene						293.095
Acrylonitrile						2278.5125
4,6-Dinitro-o-cresol						81.395
Chrysene						7130.7495
2,4-Dinitrotoluene						518.738
Cadmium			966.0734747	61889.72479		
Indeno[1,2,3-cd]pyrene			0	554835.9538		
Dibenz[a,h]anthracene			0	556826.559		
2-Methylnaphthalene	39.4212					

	CHEVRON EL SEGUNDO REFINERY		FLINT HILLS RESOURCES PINE BEND LLC		CONOCOPHILLIPS CO, ROXANA	
Pollutant Name	Total TWPE (lbs-eq/yr)	Max Allowable TWPE(lbs-eq/yr)	Total TWPE (lbs-eq/yr)	Max Allowable TWPE(lbs-eq/yr)	Total TWPE (lbs-eq/yr)	Max Allowable TWPE (lbs-eq/yr)
Sulfide	0	14308	0	10366.146	3034.92	32704
Ammonia as N	41.0300955	590.7087	5.459013072	627.1357365	12.5652	1317.5478
Chromium	7.1904	533.701	0	467.603325	12.3025	970.9
Chromium, Hexavalent	0	949.365	15.721209	262.69488	73.8531	558.45
Cyanide					1751.068291	4861.8
Zinc	1.385563595				46.75747729	
Copper	1.949918391				29.4666703	
Hexachlorobenzene	0	2843.6712				
Carbon tetrachloride	0	2035.24				
Tetrachloroethylene	0.10360751					
Chloroform	0.008182938					
Toluene	0.001244528					
Total Residual Chlorine	20.79892189				557.3766398	866.1281738
Selenium	181.4177784		3166.619378		3632.488409	
Arsenic	48.84124562				257.9093798	
Chloride			58.53525786		61.07858529	
Manganese					2411.489864	
Vanadium					157.9754074	
Mercury	0.780868422		3.530803951	9.592068165	22.4983	9636
Nickel	1.454299732				222.976409	
Polychlorinated biphenyls	0	2.056002411				
Iron					101.9745444	
Boron					125.6905635	
Barium					12.37516788	
Magnesium			484.3316521			
Potassium			188.2403889			
Chlorodibromomethane	0.04217847					
Dichlorobromomethane	0.036035732					
Antimony	0.023896159					
Xylene	0.008050476					
Methyl tert-butyl ether	0.000265491					
Beryllium	0	229.95				
Heptachlor epoxide	0	2298.40208				
1,2-Diphenylhydrazine	0	3164.915				
Heptachlor	0	2801.99988				
N-Nitrosodi-n-propylamine	0	2782.395				
2,4,6-Trichlorophenol	0	926.443				
Acrylonitrile	0	1491.39				
Bis(2-chloroethyl) ether	0	313.389				
Endrin	0	2371.478				
Toxaphene	0	43825.404				
3,3'-Dichlorobenzidine	0	1078.575				
Aldrin	0	1626.4473				
Benzidine	0	1336.946455				
Dieldrin	0	2698.2844				
Endosulfan	0	1826.095				
Thallium	0	37969.125				
Tributyltin	0	567.721				

Appendix E. TWPE

	PHILADELPHIA REFINERY		CATLETTSBURG REFINERY	
Pollutant Name	Total TWPE (lbs-eq/yr)	Max Allowable TWPE (lbs-eq/yr)	Total TWPE (lbs-eq/yr)	Max Allowable TWPE (lbs-eq/yr)
Sulfide	5053.048	15738.8	3774.288	30660
Ammonia as N	6.667412058	255.2445	4.3561284	817.18755
Chromium	0	217.175	5.65348	613.2
Chromium, Hexavalent	0	130.305	51.10098	383.469
Zinc			0.050220343	
Hexachlorobenzene	2330.010065			
Lead	0	2436.950597		
Benzene	0	51.74607035		
Phenol	0	172.4869012		
Naphthalene	0	196.6350673		
Total Residual Chlorine			0	39.37887463
Fluoride	846.78	7095.6		
Polychlorinated biphenyls	84.7244371			
Iron	18.96670479		74.30160352	

	GARYVILLE REFINERY		BATON ROUGE REFINERY		BEAUMONT REFINERY		FLINT HILLS RESOURCES, LP - EAST PLANT	
Pollutant Name	Total TWPE (lbs-eq/yr)	Max Allowable TWPE (lbs-eq/yr)	Total TWPE (lbs-eq/yr)	Max Allowable TWPE (lbs-eq/yr)	Total TWPE (lbs-eq/yr)	Max Allowable TWPE (lbs-eq/yr)	Total TWPE (lbs-eq/yr)	Max Allowable TWPE (lbs-eq/yr)
Sulfide	1615.6	17067.4	6231.96	35565.6	5670.334616		0	1941.8
Ammonia as N	21.51735	764.9232	6.358376	1275.4122	22.95784822		0	59.1519
Chromium	28.105	894.25	0	1688.855	0	892.6182112	0	68.985
Chromium, Hexavalent	74.46	521.22	0	1061.055	0	650.3361253	0	45.23445
Zinc			40.94895652				0.271936943	
Copper			39.255499					
Hexachlorobenzene	7109.178	42655.068						
Benzo[a]pyrene	367.409	367.409						
Chrysene	113.1865	113.1865						
Benz[a]anthracene	112.0185	112.0185						
Benzo(b)fluoranthene	111.909	111.909						
Benzo[k]fluoranthene	111.909	111.909						
Acrylonitrile	24.8565	24.8565						
Lead	12.85739822	128.5739822	111.8003822	42.87108047				
Anthracene	9.271	9.271						
Fluoranthene	4.672	4.672						
Fluorene	2.555	2.555						
Hexachlorobutadiene	2.2995	9.198						
Carbon tetrachloride	1.241	4.964						
Phenanthrene	1.0585	1.0585						
Di(2-ethylhexyl) phthalate	0.9125	2.7375						
Hexachloroethane	0.657	3.942						
Pyrene	0.3285	0.3285						
p-Dichlorobenzene	0.2555	1.022						
2,4-Dinitrophenol	0.148529589	1.069413038						
Acenaphthene	0.1095	0.1095						
Benzene	0.102161633	1.940972976	0	0.574166256	0.301154358	573.8259929		
Phenol	0.073	0.073						
1,2,4-Trichlorobenzene	0.073	0.438						
o-Dichlorobenzene	0.0365	0.219						
Dibutyl phthalate	0.0365	0.0365						
Nitrobenzene	0.0365	2.4455						
m-Dichlorobenzene	0.0365	0.146						
Naphthalene	0.0365	0.0365						
2,4-Dimethylphenol	0.034341535	0.034341535						
Acenaphthylene	0.030736842	0.030736842						
Dimethyl phthalate	0.012023529	0.012023529						
Diethyl phthalate	0.002510287	0.002510287						
Tetrachloroethylene	0	1.679						
1,1,2-Trichloroethane	0	0.1095						
p-Nitrophenol	0	0.089186697						
Chlorobenzene	0	0.042843213						
4,6-Dinitro-o-cresol	0	0.73						
1,1-Dichloroethane	0	0.001874709						
trans-1,2-Dichloroethylene	0	0.00033576						
Trichloroethylene	0	0.0365						
Chloroethane	0	0.034919477						
Vinyl chloride	0	2.409						
1,2-Dichloroethane	0	0.1825						
Methylene chloride	0	0.003697008						
Chloromethane	0	0.058682809						
Chloroform	0	0.022758358						
1,3-Dichloropropene	0	12.264						
1,2-Dichloropropane	0	0.657						
Toluene	0	0.020541543						
o-Nitrophenol	0	0.011845842						
1,1-Dichloroethylene	0	1.7155						
1,1,1-Trichloroethane	0	0.017153877						
Ethylbenzene	0	0.020620913						

	PASCAGOULA REFINERY		BP AMOCO WHITING REFINERY		PORT ARTHUR REFINERY		CITGO PETROLEUM CORP	
Pollutant Name	Total TWPE (lbs-eq/yr)	Max Allowable TWPE (lbs-eq/yr)	Total TWPE (lbs-eq/yr)	Max Allowable TWPE (lbs-eq/yr)	Total TWPE (lbs-eq/yr)	Max Allowable TWPE (lbs-eq/yr)	Total TWPE (lbs-eq/yr)	Max Allowable TWPE (lbs-eq/yr)
Sulfide	1783.88	31682	1941.52	23608.2	4071.844	31988.6	1528.8	20951
Ammonia as N	14.30235	82.00236	0	417.3045	9.4312815	773.8365	50.05101	1058.2518
Chromium	0	715.4	0	610.645	0	1591.765	0	835.485
Chromium, Hexavalent	0	463.5135	0	374.1615	0	1321.665	0	558.45
Cyanide					0	453.768		
Copper	2.41724	559.3917			137.75153	716.29425		
Benzo[a]pyrene							0	27996.5658
Benz[a]anthracene							0	8535.8097
Lead					657.2384	17987.2	23.59610659	62.09501735
Benzene							0.169652458	0.831629697
Total Residual Chlorine			0	3650			29.79328307	
Selenium			5494.16					
Fluoride			535.23					
Arsenic			473.8285					
Chloride			249.229607					
Manganese			74.60393					
Vanadium			25.858	1260				
Mercury			10.21447053	42.38619683	1445.4	2569.6		
Strontium			0.442867833					
Nickel	3.968	219						

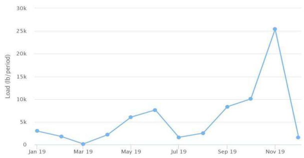
	PORT ARTHUR OIL REFINERY		GALVESTON BAY REFINERY		EXXONMOBIL REFINING & SUPPLY BAYTOWN REFINERY, BAYTOWN, TX 77520	
Pollutant Name	Total TWPE (lbs-eq/yr)	Max Allowable TWPE (lbs-eq/yr)	Total TWPE (lbs-eq/yr)	Max Allowable TWPE (lbs-eq/yr)	Total TWPE (lbs-eq/yr)	Max Allowable TWPE (lbs-eq/yr)
Sulfide	1406.72	34858.49384	0	1649.2	22176	903856.8
Ammonia as N	56.4879	837.0154769	44.9591792	2579.9952	113.72172	810.3
Chromium	1.26	3309.812448	0	61.411	0	1330.35
Chromium, Hexavalent	0	724.9759856	244.678191	40862.1657	0	1861.5
Zinc			113.07784	3839.8	888.2199989	
Aluminium			16.09870344			
Nitrogen nitrate dissolved					121.0100267	
Copper					49.83310397	

Appendix F. The identified exceedance of permssible limits

Facility Loading Calculations
TX0004871 - SHELL OIL COMPANY DEER PARK REFINERY, DEER PARK, TX 77536 2019
Monitoring Period-Level Loads for 00680 from Outfall 004

Monitoring Period Date	Pollutant Name	Outfall	Discharge Occurred?	Discharge Reported?	Discharge Estimated?	Below Detection Limit?	Measurement Type	Average Daily Value	Limit Value	Average Daily Flow (MGD)	Number of Days	Monitoring Period Load (lb/yr)	Load Over Limit	Number of Exceedances
01/31/2019	Total Organic Carbon	4	Yes	Yes	No	No	Concentration (mg/L)	7.7	70	1.49	31	2968.336723	0	0
02/28/2019	Total Organic Carbon	4	Yes	Yes	No	No	Concentration (mg/L)	12.2	70	0.62	28	1767.600148	0	0
03/31/2019	Total Organic Carbon	4	Yes	Yes	No	Yes	Concentration (mg/L)	2.5	70	0.21	31	135.8299294	0	0
04/30/2019	Total Organic Carbon	4	Yes	Yes	No	No	Concentration (mg/L)	10.5	70	0.82	30	2155.752428	0	0
05/31/2019	Total Organic Carbon	4	Yes	Yes	No	No	Concentration (mg/L)	13.9	70	1.68	31	6041.715259	0	0
06/30/2019	Total Organic Carbon	4	Yes	Yes	No	No	Concentration (mg/L)	17.7	70	1.72	30	7622.500221	0	0
07/31/2019	Total Organic Carbon	4	Yes	Yes	No	No	Concentration (mg/L)	13.7	70	0.45	31	1595.031456	0	0
08/31/2019	Total Organic Carbon	4	Yes	Yes	No	No	Concentration (mg/L)	10.9	70	0.89	31	2509.878371	0	0
09/30/2019	Total Organic Carbon	4	Yes	Yes	No	No	Concentration (mg/L)	9.4	70	3.54	30	8331.570009	0	0
10/31/2019	Total Organic Carbon	4	Yes	Yes	No	No	Concentration (mg/L)	24.9	70	1.56	31	10049.86243	0	0
11/30/2019	Total Organic Carbon	4	Yes	Yes	No	No	Concentration (mg/L)	118	70	0.86	30	25408.33407	10335.59	1
12/31/2019	Total Organic Carbon	4	Yes	Yes	No	No	Concentration (mg/L)	5.4	70	1.14	31	1592.702943	0	0

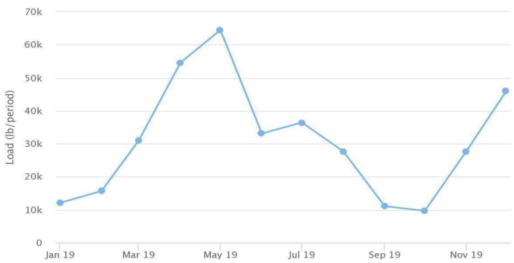
2019 Monitoring Period-Level Loads for Total Organic Carbon (00680) from Outfall 004



Facility Loading Calculations
LA0003026 - PHILLIPS 66 LAKE CHARLES REFINERY, WESTLAKE, LA 70669 2019
Monitoring Period-Level Loads for 00530 from Outfall SUM

Monitoring Period Date	Pollutant Name	Outfall	Discharge Occurred?	Discharge Reported?	Discharge Estimated?	Below Detection Limit?	Measurement Type	Average Daily Value	Limit Value	Number of Days	Monitoring Period Load (lb/yr)	Load Over Limit	Number of Exceedances
01/31/2019	Solids, total s	SUM	Yes	Yes	No	No	Quantity (kg/day)	176.8707	2102.494	31	12090	0	0
02/28/2019	Solids, total s	SUM	Yes	Yes	No	No	Quantity (kg/day)	253.9683	2102.494	28	15680	0	0
03/31/2019	Solids, total s	SUM	Yes	Yes	No	No	Quantity (kg/day)	454.4218	2102.494	31	31062	0	0
04/30/2019	Solids, total s	SUM	Yes	Yes	No	No	Quantity (kg/day)	824.0363	2102.494	30	54510	0	0
05/31/2019	Solids, total s	SUM	Yes	Yes	No	No	Quantity (kg/day)	943.3107	2102.494	31	64480	0	1
06/30/2019	Solids, total s	SUM	Yes	Yes	No	No	Quantity (kg/day)	500.2268	2147.392	30	33090	0	0
07/31/2019	Solids, total s	SUM	Yes	Yes	No	No	Quantity (kg/day)	532.8798	2147.392	31	36425	0	0
08/31/2019	Solids, total s	SUM	Yes	Yes	No	No	Quantity (kg/day)	404.9887	2147.392	31	27683	0	0
09/30/2019	Solids, total s	SUM	Yes	Yes	No	No	Quantity (kg/day)	167.3469	2147.392	30	11070	0	0
10/31/2019	Solids, total s	SUM	Yes	Yes	No	No	Quantity (kg/day)	141.4966	2147.392	31	9672	0	0
11/30/2019	Solids, total s	SUM	Yes	Yes	No	No	Quantity (kg/day)	418.5941	2147.392	30	27690	0	0
12/31/2019	Solids, total s	SUM	Yes	Yes	No	No	Quantity (kg/day)	673.0159	2147.392	31	46004	0	0

2019 Monitoring Period-Level Loads for Solids, total suspended (00530) from Outfall SUM



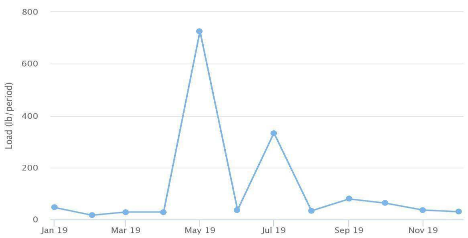
Facility Loading Calculations
PA0011533 - PHILA ENERGY SOL REF/ PES, PHILADELPHIA, PA 19145-5208 2019
Monitoring Period-Level Loads for 00745 from Outfall 015

Monitoring Period Date	Pollutant Name	Outfall	Discharge Occurred?	Discharge Reported?	Discharge Estimated?	Below Detection Limit?	Measurement Type	Average Daily Value	Limit Value	Average Daily Flow (MGD)	Number of Days	Monitoring Period Load (lb/yr)	Load Over Limit
01/31/2019	Sulfide	15	Yes	Yes	No	No	Quantity (kg/day)	0.798186	3.492063	7.53	31	54.56	0
02/28/2019	Sulfide	15	Yes	Yes	No	Yes	Quantity (kg/day)	0.612245	3.492063	6.75	28	37.8	0
03/31/2019	Sulfide	15	Yes	No	Yes	No	Quantity (kg/day)	0	3.492063	7.14	31	0	0
04/30/2019	Sulfide	15	Yes	No	Yes	No	Quantity (kg/day)	0	3.492063	6.34	30	0	0
05/31/2019	Sulfide	15	Yes	No	Yes	No	Quantity (kg/day)	0	3.492063	6.84	31	0	0
06/30/2019	Sulfide	15	Yes	No	Yes	No	Quantity (kg/day)	0	3.492063	7.06	30	0	0
07/31/2019	Sulfide	15	Yes	No	Yes	No	Quantity (kg/day)	0	3.492063	7.05	31	0	0
08/31/2019	Sulfide	15	Yes	No	Yes	No	Quantity (kg/day)	0	3.492063	4.63	31	0	0
09/30/2019	Sulfide	15	Yes	Yes	No	Yes	Quantity (kg/day)	1.952381	3.492063	3.78	30	129.15	0
10/31/2019	Sulfide	15	Yes	Yes	No	No	Quantity (kg/day)	7.315193	3.492063	3.91	31	500.03	261.33
11/30/2019	Sulfide	15	Yes	Yes	No	No	Quantity (kg/day)	1.378685	3.492063	3.23	30	91.2	0
12/31/2019	Sulfide	15	Yes	Yes	No	No	Quantity (kg/day)	1.310658	3.492063	3.72	31	89.59	0

Facility Loading Calculations
TX0005991 - PREMCOR REFINING GROUP INC - PORT ARTHUR REFINERY, PORT ARTHUR, TX 77640 2019 Monitoring Period-Level Loads for 00745 from Outfall 001

Monitoring Period Date	Pollutant Name	Outfall	Discharge Occurred?	Discharge Reported?	Discharge Estimated?	Below Detection Limit?	Measurement Type	Average Daily Value	Limit Value	Average Daily Flow (MGD)	Number of Days	Monitoring Period Load (lb/yr)	Load Over Limit	Number of Exceedances
01/31/201	Sulfide	1	Yes	Yes	No	No	Quantity (kg/day)	0.671202	14.19501	17.8	31	45.88	0	0
02/28/201	Sulfide	1	Yes	Yes	No	No	Quantity (kg/day)	0.263039	14.19501	7.1	28	16.24	0	0
03/31/201	Sulfide	1	Yes	Yes	No	No	Quantity (kg/day)	0.417234	14.19501	7.9	31	28.52	0	0
04/30/201	Sulfide	1	Yes	Yes	No	No	Quantity (kg/day)	0.430839	14.19501	9.5	30	28.5	0	0
05/31/201	Sulfide	1	Yes	Yes	No	No	Quantity (kg/day)	10.61224	14.19501	11.8	31	725.4	0	3
06/30/201	Sulfide	1	Yes	Yes	No	No	Quantity (kg/day)	0.548753	14.19501	14.6	30	36.3	0	0
07/31/201	Sulfide	1	Yes	Yes	No	No	Quantity (kg/day)	4.875283	14.19501	16.6	31	333.25	0	3
08/31/201	Sulfide	1	Yes	Yes	No	No	Quantity (kg/day)	0.485261	14.19501	12.6	31	33.17	0	0
09/30/201	Sulfide	1	Yes	Yes	No	No	Quantity (kg/day)	1.192744	14.19501	26.4	30	78.9	0	0
10/31/201	Sulfide	1	Yes	Yes	No	No	Quantity (kg/day)	0.9161	14.19501	16.2	31	62.62	0	0
11/30/201	Sulfide	1	Yes	Yes	No	No	Quantity (kg/day)	0.544218	14.19501	13.3	30	36	0	0
12/31/201	Sulfide	1	Yes	Yes	No	No	Quantity (kg/day)	0.430839	14.19501	9.4	31	29.45	0	0

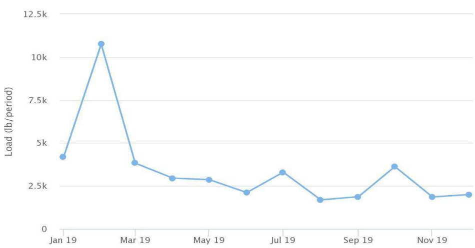
2019 Monitoring Period–Level Loads for Sulfide (00745) from Outfall 001



Facility Loading Calculations
PA0011533 - PHILA ENERGY SOL REF/ PES, PHILADELPHIA, PA 19145-5208 2019
Monitoring Period-Level Loads for 00556 from Outfall 015

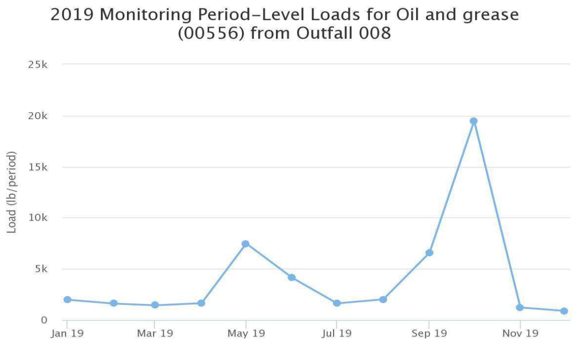
Monitoring Period Date	Pollutant Name	Outfall	Discharge Occurred?	Discharge Reported?	Discharge Estimated?	Below Detection Limit?	Measurement Type	Average Daily Value	Limit Value	Average Daily Flow (MGD)	Number of Days	Monitoring Period Load (lb/yr)	Load Over Limit	Number of Exceedances
01/31/2019	Oil and grease	15	Yes	Yes	No	Yes	Quantity (kg/day)	61.22449	200.4535	7.53	31	4185	0	0
02/28/2019	Oil and grease	15	Yes	Yes	No	No	Quantity (kg/day)	174.1497	200.4535	6.75	28	10752	0	1
03/31/2019	Oil and grease	15	Yes	Yes	No	Yes	Quantity (kg/day)	56.00907	200.4535	7.14	31	3828.5	0	0
04/30/2019	Oil and grease	15	Yes	Yes	No	Yes	Quantity (kg/day)	44.6712	200.4535	6.34	30	2955	0	0
05/31/2019	Oil and grease	15	Yes	Yes	No	Yes	Quantity (kg/day)	41.95011	200.4535	6.84	31	2867.5	0	0
06/30/2019	Oil and grease	15	Yes	Yes	No	Yes	Quantity (kg/day)	31.97279	200.4535	7.06	30	2115	0	0
07/31/2019	Oil and grease	15	Yes	Yes	No	Yes	Quantity (kg/day)	48.29932	200.4535	7.05	31	3301.5	0	0
08/31/2019	Oil and grease	15	Yes	Yes	No	Yes	Quantity (kg/day)	24.71655	200.4535	4.63	31	1689.5	0	0
09/30/2019	Oil and grease	15	Yes	Yes	No	Yes	Quantity (kg/day)	28.34467	200.4535	3.78	30	1875	0	0
10/31/2019	Oil and grease	15	Yes	Yes	No	No	Quantity (kg/day)	53.06122	200.4535	3.91	31	3627	0	0
11/30/2019	Oil and grease	15	Yes	Yes	No	Yes	Quantity (kg/day)	28.11791	200.4535	3.23	30	1860	0	0
12/31/2019	Oil and grease	15	Yes	Yes	No	Yes	Quantity (kg/day)	29.2517	200.4535	3.72	31	1999.5	0	0

2019 Monitoring Period–Level Loads for Oil and grease (00556) from Outfall 015



Facility Loading Calculations
TX0004871 - SHELL OIL COMPANY DEER PARK REFINERY, DEER PARK, TX 77536 2019 Monitoring Period-Level Loads for 00556 from Outfall 008

Monitoring Period Date	Pollutant Name	Outfall	Discharge Occurred?	Discharge Reported?	Discharge Estimated?	Below Detection Limit?	Measurement Type	Average Daily Value	Limit Value	Average Daily Flow (MGD)	Number of Days	Monitoring Period Load (lb/yr)	Load Over Limit	Number of Exceedances
01/31/201	Oil and gre	8	Yes	Yes	No	Yes	Concentration (mg/L)	2.5	15	3.06	31	1979.236114	0	0
02/28/201	Oil and gre	8	Yes	Yes	No	Yes	Concentration (mg/L)	2.5	15	2.74	28	1600.748415	0	0
03/31/201	Oil and gre	8	Yes	Yes	No	Yes	Concentration (mg/L)	2.5	15	2.21	31	1429.448304	0	0
04/30/201	Oil and gre	8	Yes	Yes	No	Yes	Concentration (mg/L)	2.5	15	2.62	30	1639.974263	0	0
05/31/201	Oil and gre	8	Yes	Yes	No	Yes	Concentration (mg/L)	2.5	15	11.56	31	7477.114208	0	0
06/30/201	Oil and gre	8	Yes	Yes	No	Yes	Concentration (mg/L)	2.5	15	6.57	30	4112.454544	0	0
07/31/201	Oil and gre	8	Yes	Yes	No	Yes	Concentration (mg/L)	2.5	15	2.5	31	1617.022969	0	0
08/31/201	Oil and gre	8	Yes	Yes	No	Yes	Concentration (mg/L)	2.5	15	3.12	31	2018.044665	0	0
09/30/201	Oil and gre	8	Yes	Yes	No	Yes	Concentration (mg/L)	2.5	15	10.5	30	6572.415938	0	0
10/31/201	Oil and gre	8	Yes	Yes	No	No	Concentration (mg/L)	16.8	15	4.48	31	19472.57868	2086.348	1
11/30/201	Oil and gre	8	Yes	Yes	No	Yes	Concentration (mg/L)	2.5	15	1.95	30	1220.591531	0	0
12/31/201	Oil and gre	8	Yes	Yes	No	Yes	Concentration (mg/L)	2.5	15	1.36	31	879.660495	0	0



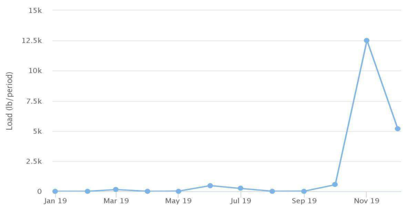
Facility Loading Calculations
PA0011533 - PHILA ENERGY SOL REF/ PES, PHILADELPHIA, PA 19145-5208 2019 Monitoring Period-Level Loads for 00530 from Outfall 015

Monitoring Period Date	Pollutant Name	Outfall	Discharge Occurred?	Discharge Reported?	Discharge Estimated?	Below Detection Limit?	Measurement Type	Average Daily Value	Limit Value	Average Daily Flow (MGD)	Number of Days	Monitoring Period Load (lb/yr)	Load Over Limit	Number of Exceedances
01/31/2019	Solids, total suspende	15	Yes	Yes	No	No	Quantity (kg/day)	76.19048	526.5306	7.53	31	5208	0	0
02/28/2019	Solids, total suspende	15	Yes	Yes	No	No	Quantity (kg/day)	66.21315	526.5306	6.75	28	4088	0	0
03/31/2019	Solids, total suspende	15	Yes	Yes	No	No	Quantity (kg/day)	55.3288	526.5306	7.14	31	3782	0	0
04/30/2019	Solids, total suspende	15	Yes	Yes	No	No	Quantity (kg/day)	48.07256	526.5306	6.34	30	3180	0	0
05/31/2019	Solids, total suspende	15	Yes	Yes	No	No	Quantity (kg/day)	71.65533	526.5306	6.84	31	4898	0	0
06/30/2019	Solids, total suspende	15	Yes	Yes	No	No	Quantity (kg/day)	45.35147	526.5306	7.06	30	3000	0	0
07/31/2019	Solids, total suspende	15	Yes	Yes	No	No	Quantity (kg/day)	81.17914	526.5306	7.05	31	5549	0	0
08/31/2019	Solids, total suspende	15	Yes	Yes	No	No	Quantity (kg/day)	399.093	526.5306	4.63	31	27280	0	1
09/30/2019	Solids, total suspende	15	Yes	Yes	No	No	Quantity (kg/day)	49.43311	526.5306	3.78	30	3270	0	0
10/31/2019	Solids, total suspende	15	Yes	Yes	No	No	Quantity (kg/day)	56.68934	526.5306	3.91	31	3875	0	0
11/30/2019	Solids, total suspende	15	Yes	Yes	No	No	Quantity (kg/day)	145.5782	526.5306	3.23	30	9630	0	0
12/31/2019	Solids, total suspende	15	Yes	Yes	No	No	Quantity (kg/day)	115.1927	526.5306	3.72	31	7874	0	0

Facility Loading Calculations
TX0006904 - VALERO CORPUS CHRISTI REFINERY EAST PLANT, CORPUS CHRISTI, TX 78407
2019 Monitoring Period-Level Loads for 00610 from Outfall 001

Monitoring Period Date	Pollutant Name	Outfall	Discharge Occurred?	Discharge Reported?	Discharge Estimated?	Measurement Type	Average Daily Value	Limit Value	Average Daily Flow (MGD)	Number of Days	Monitoring Period Load (lb/yr)	Load Over Limit	Contains Potential Outliers?	Number of Exceedances
01/31/2019	Ammonia as	1	Yes	Yes	No	Quantity (kg/day)	0.04535147	126.0770975	1.24	31	3.1	0	No	0
02/28/2019	Ammonia as	1	Yes	Yes	No	Quantity (kg/day)	0.09070295	126.0770975	1.24	28	5.6	0	No	0
03/31/2019	Ammonia as	1	Yes	Yes	No	Quantity (kg/day)	2.13151927	126.0770975	1.241	31	145.7	0	No	0
04/30/2019	Ammonia as	1	Yes	Yes	No	Quantity (kg/day)	0.04535147	126.0770975	1.26	30	3	0	No	0
05/31/2019	Ammonia as	1	Yes	Yes	No	Quantity (kg/day)	0.27210884	126.0770975	1.21	31	18.6	0	No	0
06/30/2019	Ammonia as	1	Yes	Yes	No	Quantity (kg/day)	7.16553288	126.0770975	1.24	30	474	0	No	0
07/31/2019	Ammonia as	1	Yes	Yes	No	Quantity (kg/day)	3.44671202	126.0770975	1.125	31	235.6	0	No	0
08/31/2019	Ammonia as	1	Yes	Yes	No	Quantity (kg/day)	0.13605442	126.0770975	1.16	31	9.3	0	No	0
09/30/2019	Ammonia as	1	Yes	Yes	No	Quantity (kg/day)	0.27210884	126.0770975	1.78	30	18	0	No	0
10/31/2019	Ammonia as	1	Yes	Yes	No	Quantity (kg/day)	8.02721088	126.0770975	1.09	31	548.7	0	No	0
11/30/2019	Ammonia as	1	Yes	Yes	No	Quantity (kg/day)	189.251701	126.0770975	1.5	30	12519	4179	Yes	2
12/31/2019	Ammonia as	1	Yes	Yes	No	Quantity (kg/day)	76.1451247	126.0770975	1.639	31	5204.9	0	Yes	0

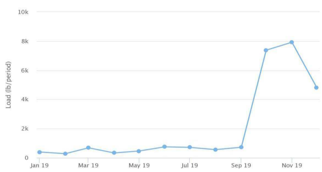
2019 Monitoring Period–Level Loads for Ammonia as N (00610) from Outfall 001



Facility Loading Calculations
TX0006904 - VALERO CORPUS CHRISTI REFINERY EAST PLANT, CORPUS CHRISTI, TX 78407
2019 Monitoring Period-Level Loads for 00310 from Outfall 001

Monitoring Period Date	Pollutant Name	Outfall	Discharge Occurred?	Discharge Reported?	Discharge Estimated?	Below Detection Limit?	Measurement Type	Average Daily Value	Limit Value	Average Daily Flow (MGD)	Number of Days	Monitoring Period Load (lb/yr)	Load Over Limit	Number of Exceedances
01/31/2019	BOD, 5-day, 20 d	1	Yes	Yes	No	No	Quantity (kg/day)	5.804989	189.5692	1.24	31	396.8	0	0
02/28/2019	BOD, 5-day, 20 d	1	Yes	Yes	No	No	Quantity (kg/day)	4.535147	189.5692	1.24	28	280	0	0
03/31/2019	BOD, 5-day, 20 d	1	Yes	Yes	No	No	Quantity (kg/day)	9.977324	189.5692	1.241	31	682	0	0
04/30/2019	BOD, 5-day, 20 d	1	Yes	Yes	No	No	Quantity (kg/day)	4.988662	189.5692	1.26	30	330	0	0
05/31/2019	BOD, 5-day, 20 d	1	Yes	Yes	No	No	Quantity (kg/day)	6.802721	189.5692	1.21	31	465	0	0
06/30/2019	BOD, 5-day, 20 d	1	Yes	Yes	No	No	Quantity (kg/day)	11.33787	189.5692	1.24	30	750	0	0
07/31/2019	BOD, 5-day, 20 d	1	Yes	Yes	No	No	Quantity (kg/day)	10.43084	189.5692	1.125	31	713	0	0
08/31/2019	BOD, 5-day, 20 d	1	Yes	Yes	No	No	Quantity (kg/day)	8.163265	189.5692	1.16	31	558	0	0
09/30/2019	BOD, 5-day, 20 d	1	Yes	Yes	No	No	Quantity (kg/day)	10.88435	189.5692	1.78	30	720	0	0
10/31/2019	BOD, 5-day, 20 d	1	Yes	Yes	No	No	Quantity (kg/day)	107.9365	189.5692	1.09	31	7378	0	1
11/30/2019	BOD, 5-day, 20 d	1	Yes	Yes	No	No	Quantity (kg/day)	119.7732	189.5692	1.5	30	7923	0	1
12/31/2019	BOD, 5-day, 20 d	1	Yes	Yes	No	No	Quantity (kg/day)	70.29478	189.5692	1.639	31	4805	0	0

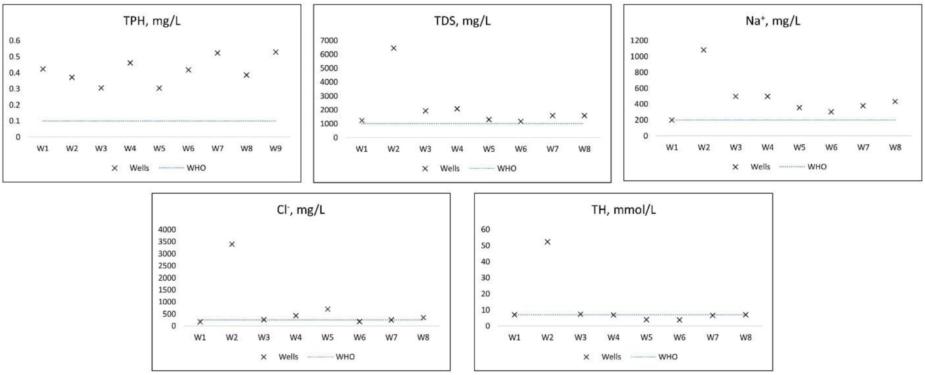
2019 Monitoring Period–Level Loads for BOD, 5–day, 20 deg. C (00310) from Outfall 001



Appendix G. Statistics of wastewater quality of European refineries. (CONCAWE 2020)

Analyte	Number of Sites (Reported)	Average Annual Concentration (mg/L)	Industry Total Effluent Load (t)
Organics			
Oil in Water (OiW) or Total Petroleum Hydrocarbons (TPH)	54	1.42	257.1
Phenol Index	44	0.084	29.6
Total Benzene, Toluene, Ethylbenzene and Xylene (BTEX)	61	0.023	6.6
Total Polyaromatic Hydrocarbons (PAHs)	28	0.0004	0.04
General parameters			
Total Nitrogen	51	8.57	1,855.8
Total Phosphorus	52	0.78	157.9
Biochemical Oxygen Demand (BOD)	54	14.7	2,396.6
Chemical Oxygen Demand (COD)	64	64.0	16,150.9
Total Organic Carbon (TOC)	39	13.1	1,499.6
Total Suspended solids (TSS)	62	15.1	4,098.4
Metals			
Cadmium	48	0.003	0.62
Lead	47	0.006	1.12
Mercury	45	0.004	0.39
Nickel	47	0.012	2.87
Vanadium	27	0.05	8.09

Appendix H Groundwater quality around the receiver of refineries' wastewater compared to WHO limits (Radelyuk et al. 2020)



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